


DIATOM EVIDENCE OF  
ENVIRONMENTAL CHANGES  
IN WETLANDS



CAPE COD NATIONAL SEASHORE



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DIATOM EVIDENCE OF ENVIRONMENTAL CHANGES IN WETLANDS:  
CAPE COD NATIONAL SEASHORE

Part I. Prehistoric and Historic Trends in Acidity of the Outer Cape Ponds

Part II. Comparison of Two Estuaries: Herring River in Wellfleet,  
and Pamet River in Truro

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December, 1985

Part I.

PREHISTORIC AND HISTORIC TRENDS IN ACIDITY  
OF THE KETTLE PONDS IN THE CAPE COD NATIONAL SEASHORE

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## 1. EXECUTIVE SUMMARY

In this study, the relationship between modern diatom assemblages and the modern chemistry of the ponds in the Cape Cod National Seashore in south-eastern Massachusetts, is used to reconstruct the 12,000-year pH history of Duck Pond, an acid, oligotrophic kettle pond.

The kettle ponds in the Cape Cod National Seashore are set in non-calcareous, non-weathering, crystalline outwash sands and have low specific conductance, low alkalinity, and generally clear water. These factors make them sensitive to acid and toxic deposition because they receive most of their nutrients from the atmosphere. The 15 Outer Cape ponds chosen for study range in pH from 4.3 to 7.5 and are broadly representative of the more than 180 ponds on the Cape (with a pH range of 4.1 to 8.3). The ponds can be divided into three groups: ponds with a pH below 5, those with moderate pH values from 5 to 6.8, and ponds with some tidal influence and pH values higher than 6.8.

Examination of recent pondwater pH shows that the pH increased about 0.3 pH units in several of the ponds from low values in 9/75 and 4/82 and has then remained relatively stable. This stability is documented by monthly pH measurements taken during the past two years. Precipitation pH, on the other hand, has varied greatly during the past 4 years, ranging between very low (less than pH 3.5) to moderate (more than pH 5.6) values. The precipitation on the Outer Cape contains abundant seawater ions as well as high nitrates and sulfates during the lowest pH events. Although there is no apparent seasonality to low pH precipitation events, increased summer use of the ponds provides alkaline inputs which balance some of the acidity in summer rainfall.

Diatoms in the modern sediments from the Outer Cape ponds were analyzed and divided into pH-related groups. Correlation analysis suggests that each pH-related diatom group responds to different characteristics of the ponds. Acidobiontic diatoms are correlated inversely with alkalinity, while the acidophilic and alkaliphilic diatoms are highly correlated with pH changes (but in different directions). Circumneutral diatoms are highly correlated with the % of total planktic diatoms and inversely correlated with the % of total acid diatoms, while alkalibiontic diatoms are highly correlated with specific conductance and all the seawater-associated ions and reflect the coastal environment of the Cape.

Changes in pH over the past 12,000 years in Duck Pond, S. Wellfleet, were reconstructed by regressing modern pH observations from the Outer Cape ponds against differences in modern diatom assemblages in the pond sediments. The reconstructed pH suggests that the pond has been acid for its entire history with a mean pH of  $5.2 \pm 0.3$ . The highest pH in the pond (a pH of 6) was during a period of increased windiness and erosion during late-glacial time. Although the diatom evidence indicates that Duck Pond did become more acid recently (with a mean pH of about  $4.9 \pm 0.1$  for the past 150 years), the pH has varied both up and down throughout the Holocene, and Duck Pond has had acidity as low as the present at other times in the past 12,000 years. There is significant correlation between charcoal influx and alkaline Fragilaria diatoms in the pre-European-settlement core and between percent charcoal and the total acid diatoms in the post-European-settlement core. These results reflect the fact that while wood charcoal and ash deposited in runoff from local forest fires is generally alkaline, windborne charcoal residue, gas and soot from fossil fuel combustion is quite acid. An inverse correlation between the diploxylon Pinus (pitch pine) species and the reconstructed pH and a linear correlation between haploxylon Pinus (white pine) and the alkaliphilic diatoms, suggest that changes in vegetation caused by changes in climate and fire frequency also affected the pH history of the pond.



## 2. PROBLEM STATEMENT

Because of its geologic history and setting, Cape Cod, in southeastern Massachusetts, is one of the regions sensitive to the effects of acid deposition (Fig. 1). It has many kettle lakes set in non-calcareous, crystalline, coarse outwash sands deposited about 17,000 to 14,000 years ago during the recession of the Laurentide ice sheet. The ponds were formed by differential melting of stagnant ice blocks. Some of these freshwater kettle ponds are within the Cape Cod National Seashore and comprise a unique, diverse, and nationally important resource that should be carefully preserved (Fig 2). There is need for a definitive study of the prehistoric and historic acidity levels of the Seashore ponds because:

1. There is current concern for the effects of acid rain on poorly buffered kettle ponds.
2. There is preliminary evidence that some of the Seashore ponds have always been acid.
3. The Commonwealth of Massachusetts wishes to initiate a program "treating" acid-degraded ponds with lime to raise the pH. This kind of treatment would result in degradation of naturally-acid lake ecosystems. Therefore, some knowledge of the natural variation of the pH within these ponds is necessary so that sensible management decisions can be made. Ponds that are naturally-acidified should be identified, as well as those undergoing anthropogenic acidification and/or toxification.
4. Very few long-term lake pH histories have been analyzed. However, the results from short-term histories of lake pH (covering the past 100 to 200 years) suggest that lake acidification is not synchronous, even within a region, and the causes of acidification and/or lake degradation are not that clear.

With these problems and goals in mind, I have reconstructed the 12,000-year pH history of Duck Pond in South Wellfleet, Massachusetts. I have used modern diatom assemblages and modern chemical data from lakes in the Cape Cod National Seashore in the Outer Cape (Eastham, Wellfleet, Truro, and Provincetown)(Fig. 1 and 2, Table 1), an area of about 36 km x 4 km in extent, to provide modern analogs in order to construct a transfer function for pH.

## 3. PROBLEM BACKGROUND

Transport of acid-laden plumes of air from industrial areas to other regions has been documented by chemical analysis since the 1950's. Although it is believed that recent increases in acid precipitation have caused major problems in wetlands in sensitive regions of North America that are downwind of highly industrialized areas, the U. S. and Canada have only recently set up monitoring networks to analyze patterns and trends of toxic atmospheric pollution. Areas most affected by acid precipitation are the Adirondacks in New York, New England, and, increasingly, the southeastern and western states.

Rainwater has a natural pH of 5.6 (although recent studies indicate that unpolluted precipitation may have a wider natural range), but consistent annual values of as low as pH 4.2 have been measured in sensitive regions and acid precipitation events with pH of 2 or 3 have been monitored. Because of continuous acid deposition, poorly buffered lakes in areas with non-calcareous crystalline rocks or those with abundant trace metals that can be weathered out of surrounding rocks (Al, Zn, Cu, Cd, Se) by acid rainwater, are believed to have become more acid and/or more contaminated with toxic trace elements. In certain lakes, this situation leads to changes in phytoplankton and zooplankton and to loss of amphibian and fish populations. Many fish cannot

reproduce in water with a pH lower than 5.6, although there are naturally-acid lakes with genetically-adapted populations of acid-tolerant fish.

In addition, acid and other toxic atmospheric deposition has injured and killed people (London smog, Belgium smog, Donora, Pennsylvania smog) and destroyed forests, foodcrops, and buildings (limestone, marble, stained glass, paintings) as well as wetlands. It is an international problem and one in which the countries or regions producing the most pollution are, in many cases, separate from the countries and regions most affected by atmospheric deposition. As far as wetland ecosystem damage goes, acid degradation of lakes has been documented in Scotland and England, the Netherlands, and Scandinavia.

In North America there is documentation of increased nitrates and sulfates in the precipitation coming from air masses from industrialized areas. But even though recent lake damage is indicated in some studies, the cause of with-in lake changes such as the disappearance of fish, is not that clear. Several questions must still be answered:

1. What lakes or sets of lakes have become acidified?
2. When did acidification of the individual lake system begin and what was the history and range of pH variation in the lake? This information cannot be elicited by comparing the immediate pre- and post-European settlement changes. The disturbance history of the lake and the long-term pH trends, as well as evidence for naturally-occurring "reversals," must be determined.
3. What caused the acidification and what is meant by an acidified lake? Is this different from an acid-degraded lake?
4. When has acidity gone "too far?" Is this a question of our present use of/or need for the lake, or some point inherent to natural systems?
5. To what extent does low pH precipitation and acidic dryfall deposition affect lake pH?
6. What factors other than geology and soil make the relationship between precipitation pH and lake pH more "robust?" This involves knowledge of morphometry of the lake, the flushing rate of the lakewater (residence time), and the magnitude, direction, and timing (seasonality) of other impacts from various uses.
7. What can we do to solve the problem -- as a region, as a state, as a nation, or internationally?

These questions can be answered in two ways. Firstly, by a comparison of present-day chemical data with chemical analyses taken in the past, and secondly, by analysis of the continuous record of historical and prehistorical environmental change found in lake sediments. Unfortunately, there is very little reliable old chemical data and in even recent efforts there are important missing variables. In the 208 Water Quality Survey of Massachusetts lakes conducted in 1975 and 1976, no sulfate determinations were made and no minerology of the lakewater (no Al, Cd, etc.) was measured. But lake sediment cores containing fossil assemblages can be compared to arrays of modern assemblages and then correlated with modern chemical data. In this way inferences about the past can be made.

Algal fossils provide with-in lake information most relevant to lake acidification. In most lake environments, the frustules of diatoms (Bacillariophyta), algae with silica cell walls, are abundant and well-preserved. Diatoms have also been the object of much taxonomic and ecologic study.

Diatom associations integrate pond pH. The accumulation of diatom frustules in the lake sediments represents the annual or decadal response of the biota in the lake. Seasonal and microhabitat variation are smoothed at



medium frequency sampling intervals. Diatoms respond relatively rapidly to environmental changes such as pH, and also to salinity gradients and to changes in nutrient availability, water levels, and temperature. Diatoms are therefore reliable variables with which to reconstruct the environmental history of a lake, in general, and the pH changes within a lake, in particular. Correlation of chemical variables, morphometric factors, disturbance indicators, and pollen and diatom percentages, enable separation of some of these factors affecting diatom distribution from those caused by change in lakewater pH.

Pollen analysis and radiocarbon dating of the sediments are necessary to provide a framework for diatom analysis of the lake cores. These techniques provide a history of regional vegetation and climate change and establish pre- and post-European-settlement boundaries and the timing of other well-defined pollen horizons. When choosing a site for diatom analysis, availability of modern chemical data is also crucial, as is an array of lakes in a similar geologic setting with a wider range of pH and other chemistry, so that all possible downcore variations in the history of the lake being studied will be taken into account.

#### 4. RESEARCH RESULTS AND APPLICATIONS

Major results and conclusions from this study:

1. Duck Pond, and the other acid ponds of the Outer Cape, are extremely sensitive to local and atmospheric inputs because of their geologic and edaphic setting. All the ponds in the Outer Cape which do not have tidal influence have very low specific conductance (less than 100 umhos/cm, Figs 3,4; Tables 1,2). Most ion deposition in the ponds comes from the atmosphere and includes abundant seawater ions (Fig 5A).

2. Definite characteristics can be described for the acid lakes on the Outer Cape. They all have high percentages of acidobiontic and acidophilic diatoms (higher than 70% total acid diatoms) (Fig 6), more than 75% periphytic diatoms (composed mainly of acid species of Eunotia, Frustulia, Pinnularia, and Navicula) (Fig 7), high nitrate levels, low specific conductance, and negative alkalinity values (Fig 3). These similarities exist even though the morphometry and trophic state (dystrophic, oligotrophic) of these ponds differ.

3. Although there is definite documentation of acid precipitation on the Cape (Figs 8,9), and of low pH in the ponds (Table 1), especially in the early 1980's, recent pond pH values have been relatively stable (Fig 4; Table 2).

4. Duck Pond has a 12,000-year history as an acid lake ecosystem with a mean pH of  $5.2 \pm 0.3$  (Fig 10,11<sup>A,B,C</sup>, Table 3).

5. Since about 150 years ago, the pH of the pond has dropped from the mean pH value of  $5.2 \pm 0.3$  about 0.3 pH units to a mean pH of  $4.95 \pm 0.1$  (Fig 12, Table 3).

6. The pond has had pH variations in the past due to vegetation, and temperature and/or water level changes. Also, atmospheric loading of acid or alkaline dust, charcoal, and gases from volcanos and forest fires, and changes in atmospheric CO<sub>2</sub> in the past, may have affected the pond over a longer period of time.

7. Duck Pond appears to be able to balance (buffer in some way) acid loadings because it has increased as well as decreased in pH in the past. The continuous salt spray from the ocean may aid in buffering, but also adds acid anions like SO<sub>4</sub><sup>-</sup> and Cl<sup>-</sup>. Duck Pond probably does not have high amounts of toxic trace metals in the drainage basin (such as aluminum) which

would, on one hand, buffer increasing acidity, but, on the other hand, is, in itself, toxic to the biota in freshwater ecosystems. (This has to be tested, but there is some negative evidence for this hypothesis. No Fragilaria acidobiontica diatoms have been found in the Duck Pond sediments nor in the modern sediments from the acid Cape ponds. This diatom has been recently identified as an acid water (pH below 5) indicator species in aluminum-enriched lakes in the Adirondacks and New England).

8. There may be a seasonality factor determining the affect of acid deposition on the Seashore ponds. When low pH rain is deposited in spring, winter, or fall, the effect of the acid loading (either by direct deposition or from seepage through the soils of the drainage basin) may be enhanced. If low pH rain comes immediately before or coincident with summer nutrient additions within the watershed, the effect of the acid on the pond is buffered (Fig 9). This would not be the case with deposition of toxic trace metals or other toxic substances -- some of them from local as well as extraregional sources -- which remain for a long time in the sediments of the lake. High lead levels measured in 1984 in Ryder Pond probably are the result of wash-in from automobile exhaust from the adjacent highway.

9. Great Pond (T), which had been limed in 1973, had a pH of 6.3 in 1975, when the other acid ponds were relatively lower, but Great Pond (T) subsequently reached a pH of about 6.3 again in recent years without further liming. Although  $\text{Ca}^{++}$  values increased after the liming in 1973, the alkalinity (generally an indication of the buffering capacity of a lake) stayed relatively constant (Fig 4).

10. The Outer Cape ponds have lakewater chemistry that is unique from pond to pond and the chemical characteristics of the aquifer are closely sensed by the diatom assemblages in the modern sediment samples from these ponds. However, this fact does not obscure the relationship between pH and the diatom pH groupings. Because the ponds exchange water with the ground, it is important to determine if these chemical differences represent aquifer differences and were always present or if they were caused more recently by settlement or development changes.

11. Diatoms are very sensitive indicators of the pH and pollution status of freshwater ponds and should be monitored on a regular basis -- possibly every other year or every five years -- especially since major development changes are occurring in the region.

12. The timing of acidification of ponds in the Northern Hemisphere is not synchronous. Present industrial emissions can increase acidity in naturally-acid ponds, but probably does not cause it. However, degradation of lake ecosystems can be caused by the increase of toxic metals released through acid weathering of soils and rocks, and by toxic chemicals (PCBs, PAHs, etc.) also found in industrial emissions as well as from acid deposition.

13. Although there is acid deposition into the Outer Cape ponds, this problem does not require immediate action such as pond manipulation. Large-scale manipulation such as liming may actually tip the balance in these delicate ecosystems and lead to problems of lake eutrophication. However, sensible environmental policies should be adopted and enforced right away by federal, as well as local governments. These policies must include strict industrial and automobile emission controls at the federal level, and zoning controls to limit erosion and prevent over-pumping and contamination of the Cape freshwater aquifer, adequate provisions for sewerage disposal, and continuous monitoring of groundwater, pond chemistry and biology, and fog aerosols, at the local level. If this is done, Duck Pond, and the other Outer Cape kettle ponds, will remain important, unique, and evolving ecosystems.

## 5. RECOMMENDED MANAGEMENT ALTERNATIVES

1. There is no immediate threat from atmospheric acid deposition to the kettle ponds of the Cape Cod National Seashore. Most of these ponds have been acid ecosystems for their entire evolutionary history. However, there may very well be more local problems caused by increased use of the ponds and the rapid recent development of the Outer Cape. Increased demand for freshwater and increased amounts of groundwater pollution will lead to lowering of water quantity and quality in the ponds. Increased traffic, combined with the unique ocean-related climate characteristics of the Outer Cape (including abundant or daily fogs) may provide toxic levels of  $\text{NO}_x$ , Pb, and other toxic elements to the ponds and the vegetation surrounding the ponds. The fog aerosols should be analyzed to determine if there are seasonal chemical changes and how these affect the Cape ecology. Monitoring diatom assemblages in the ponds already sampled would enable the Seashore to identify change, to determine the direction of change, and to measure the rate of change caused by some of these factors. By monitoring the diatoms and the chemistry of the ponds on a regular basis, a natural experiment could be conducted on these acid ponds which would yield valuable information about naturally-acid lake ecosystems.

2. In addition, because any kind of toxic atmospheric deposition is usually not a local problem, sensible local, regional, federal, and international policies to limit toxic emissions and to monitor pollution effects should be initiated as soon as possible. They should include:

- a. liming of smokestacks (not ponds), using scrubbers and filters, or whatever is necessary to limit polluting emissions.
- b. the monitoring and testing of industrial emissions for toxic compounds other than acid substances,
- c. a decrease in auto emissions (including  $\text{NO}_x$ , Pb),
- d. groundwater testing and limits on pumping of freshwater on the Cape
- e. local erosion control and sewage disposal controls
- f. no experimentation on Seashore ponds unless ecological history is known and experimental affects can be reasonably predicted.

3. The ecology of the acid Outer Cape ponds is unique. Within the memory of anyone living on the Cape today, the ponds have not been fish ponds. They should be maintained as swimming and boating ponds, because ocean fishing facilities on the Cape are abundant.



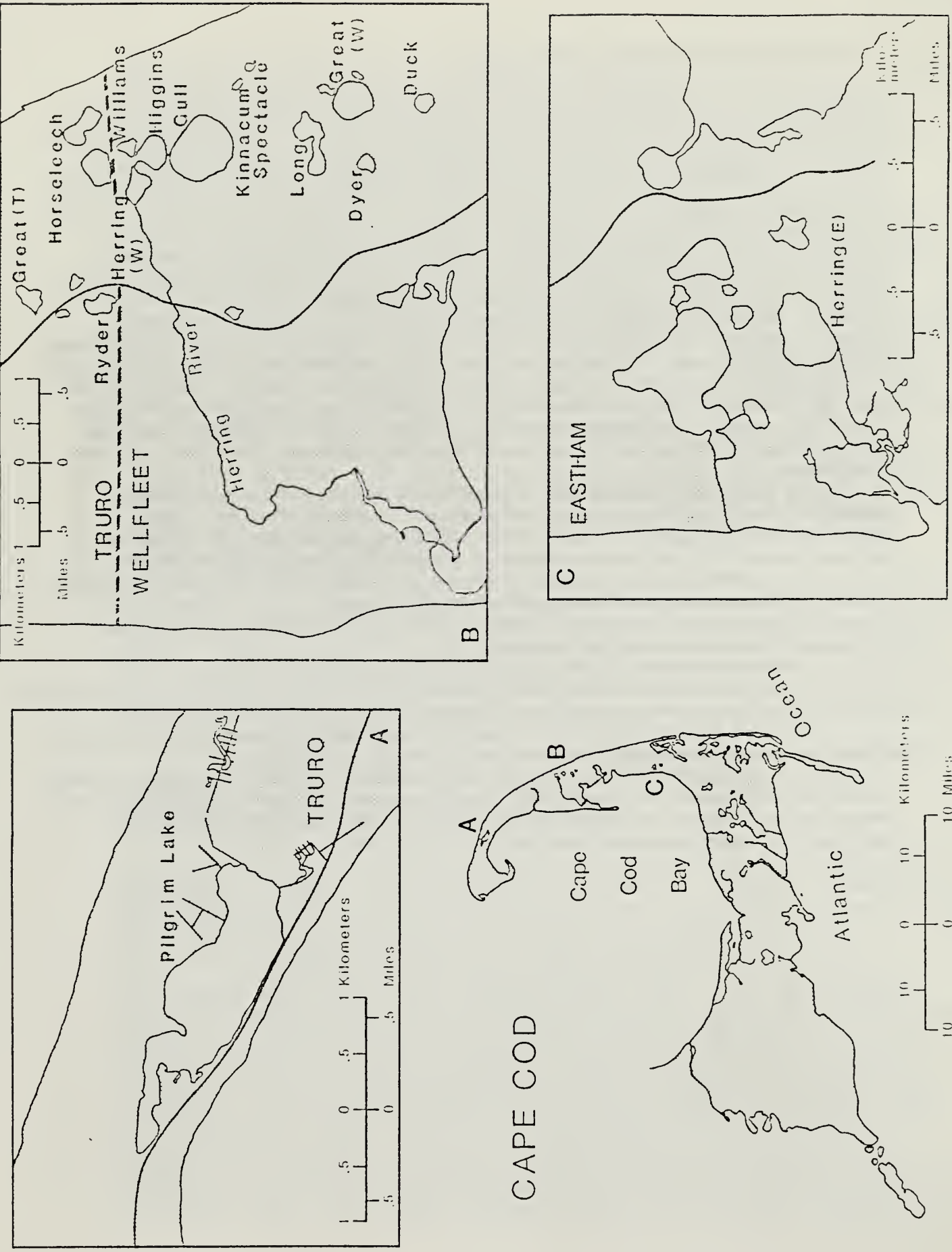


Fig. 1. Maps of Cape Cod, and Eastham, Wellfleet, Truro, Outer Cape Ponds.



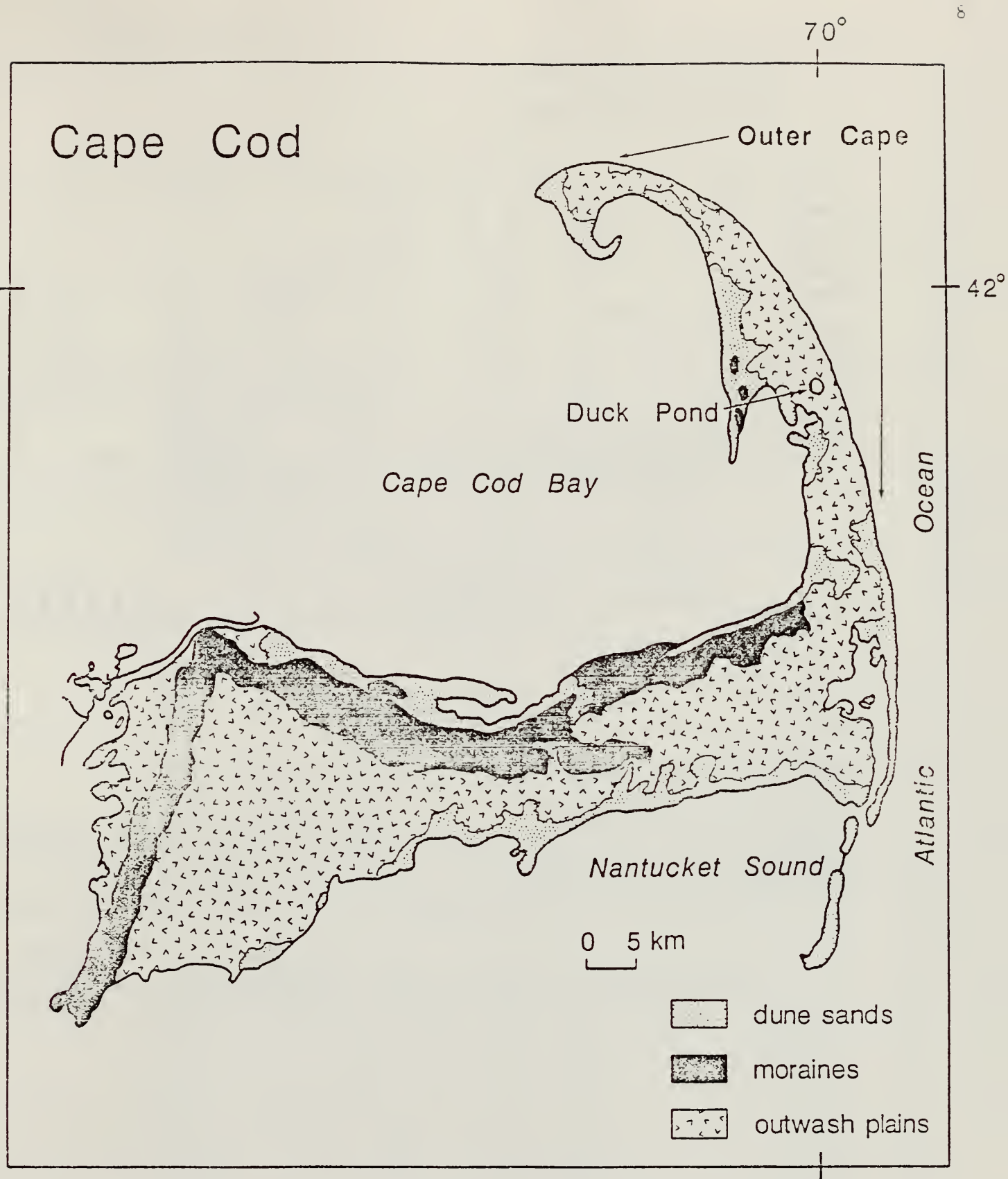


Fig. 2. Map of geologic and edaphic characteristics: Cape Cod.

Morphometric and Chemical Analysis  
Modern Sediment Samples  
Cape Cod National Seashore Ponds  
Eastham, Westfleet, and Truro, Massachusetts

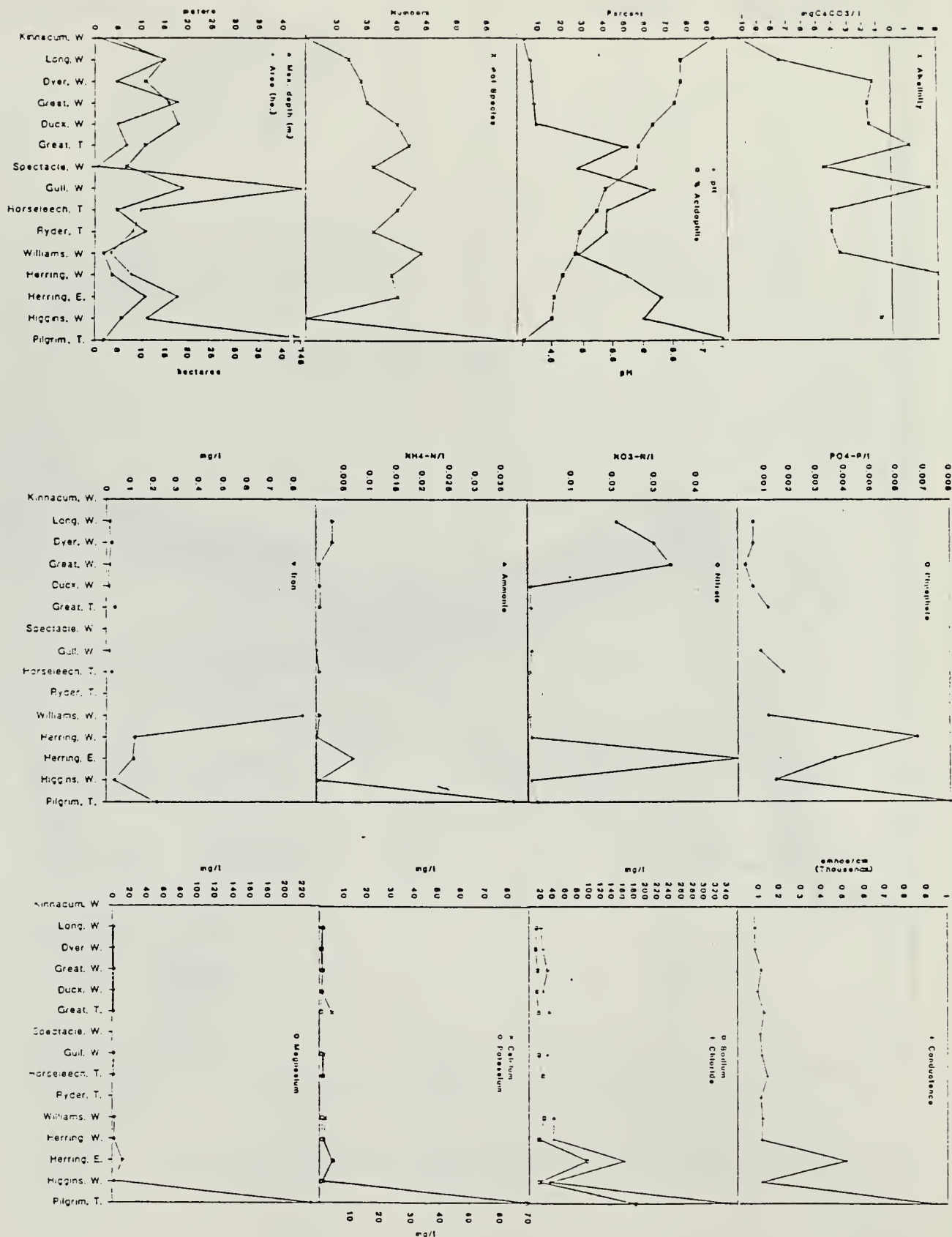
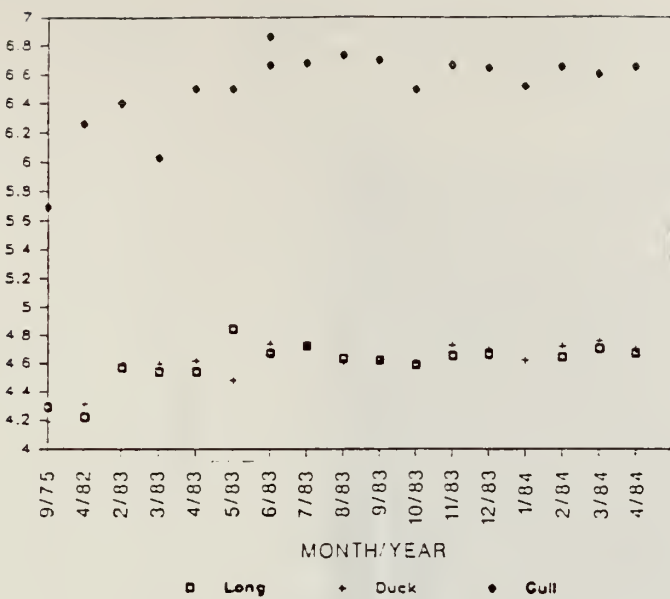
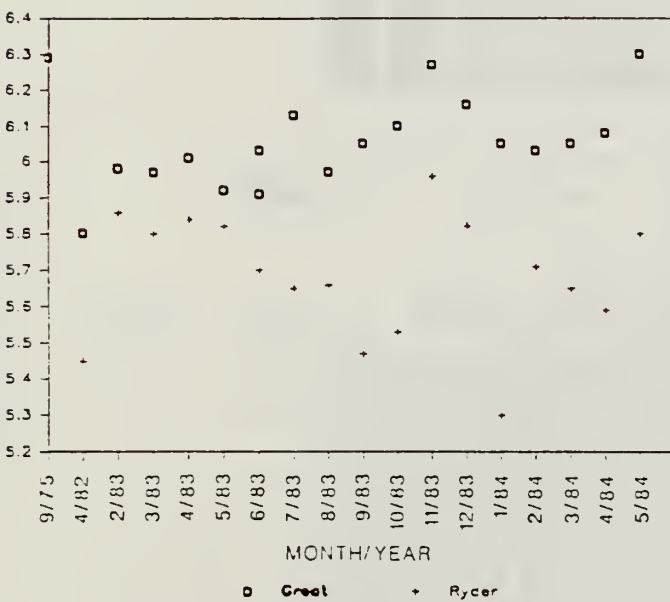


Fig. 3. Morphometry, chemistry of pondwater, and diatoms from modern sediment samples: Outer Cape Ponds. All of the ponds lie 2.5m or less above mean sea level and at about 42°N, 70°W (Fig. 2).

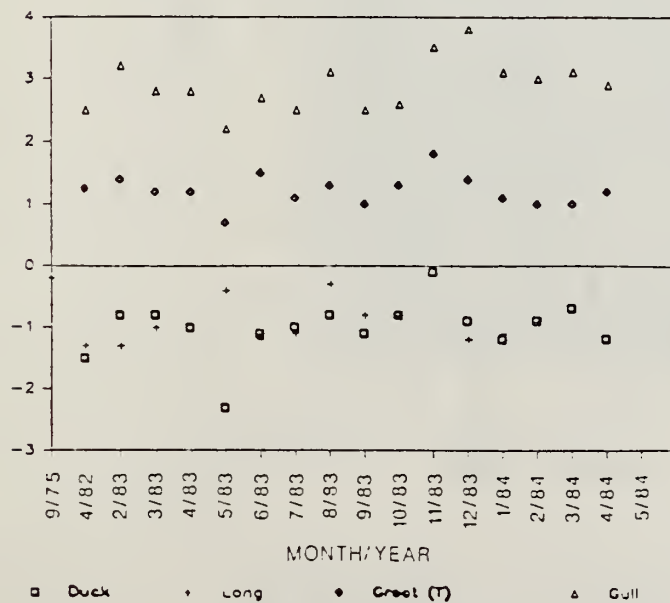
## Wellfleet Ponds: pH



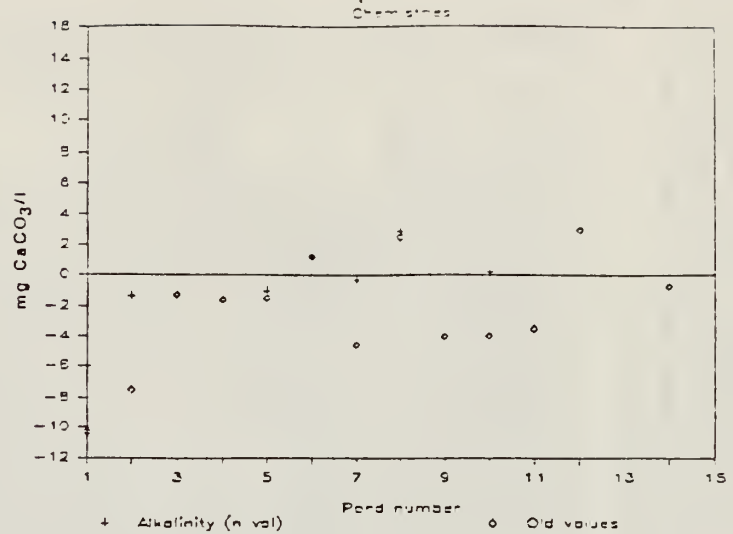
## Truro Ponds: pH



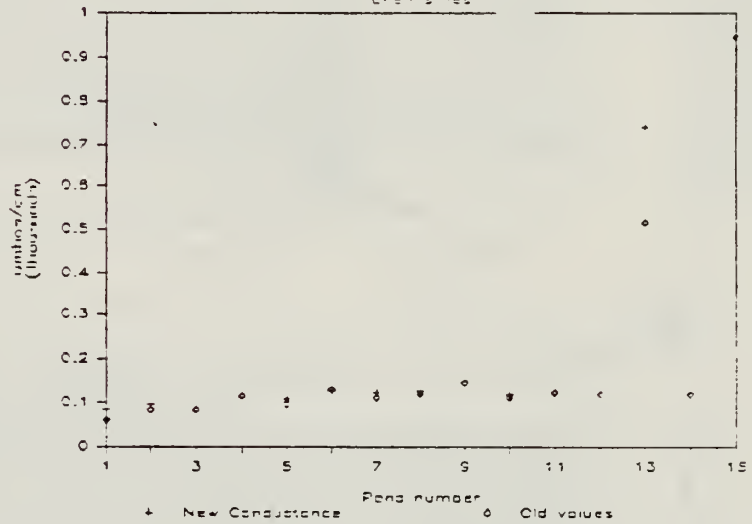
## Outer Cape Ponds: Alkalinity



## D Outer Cape Cod Ponds



## E Outer Cape Cod Ponds



## F Outer Cape Cod Ponds

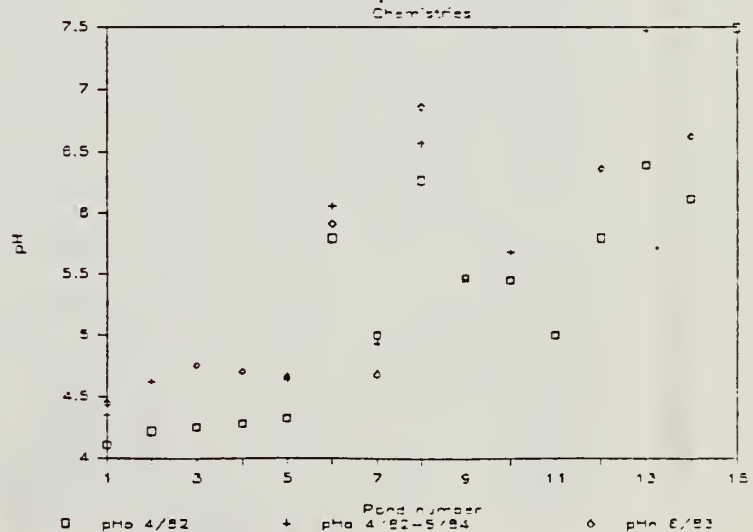
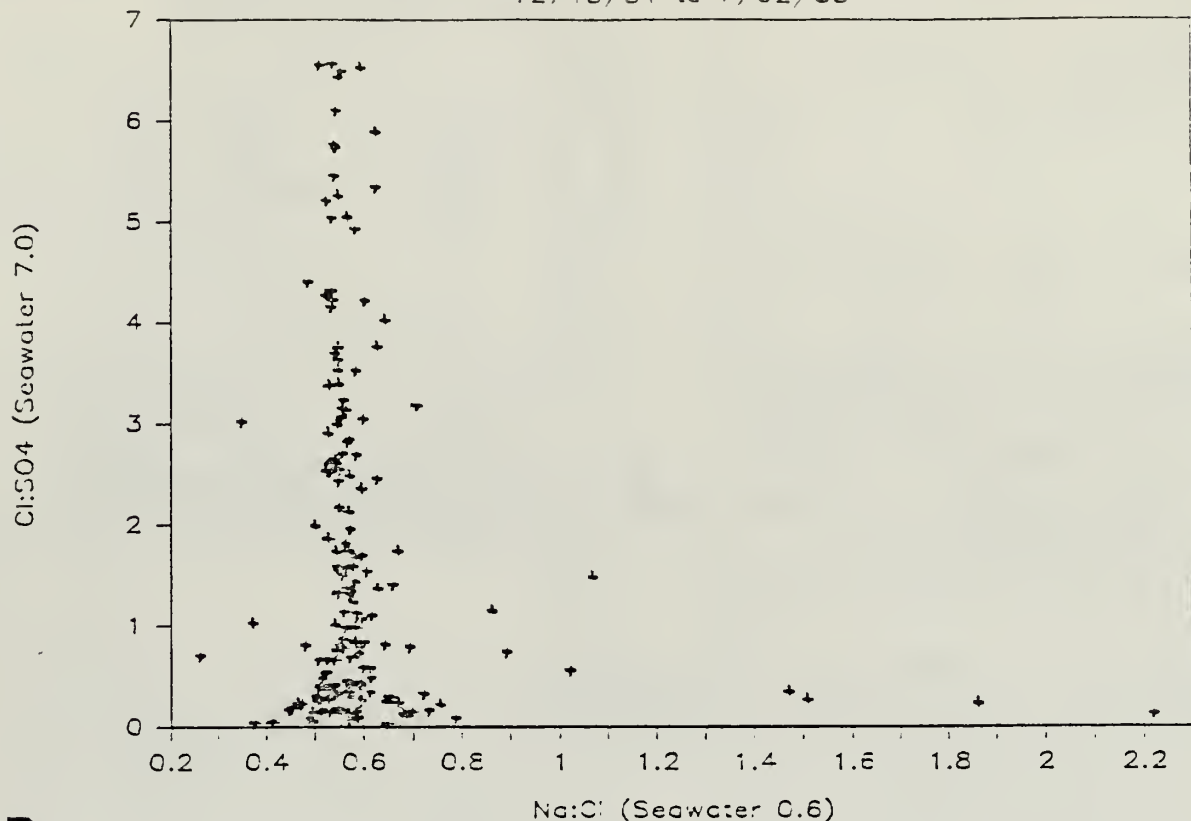


Fig. 4. A-C, pH and alkalinity measurements on some Wellfleet and Truro ponds from 9/75 through 5/84. D-F, comparison of 1982 measurements of alkalinity, conductance, and pH of all the Outer Cape Ponds. Ponds 1-15 correspond with pond order in Fig. 3.

A

# PRECIPITATION CHEMISTRY: OUTER CAPE COD

12/15/81 to 7/02/85



B

# PRECIPITATION CHEMISTRY: OUTER CAPE COD

12/15/81 to 7/02/85

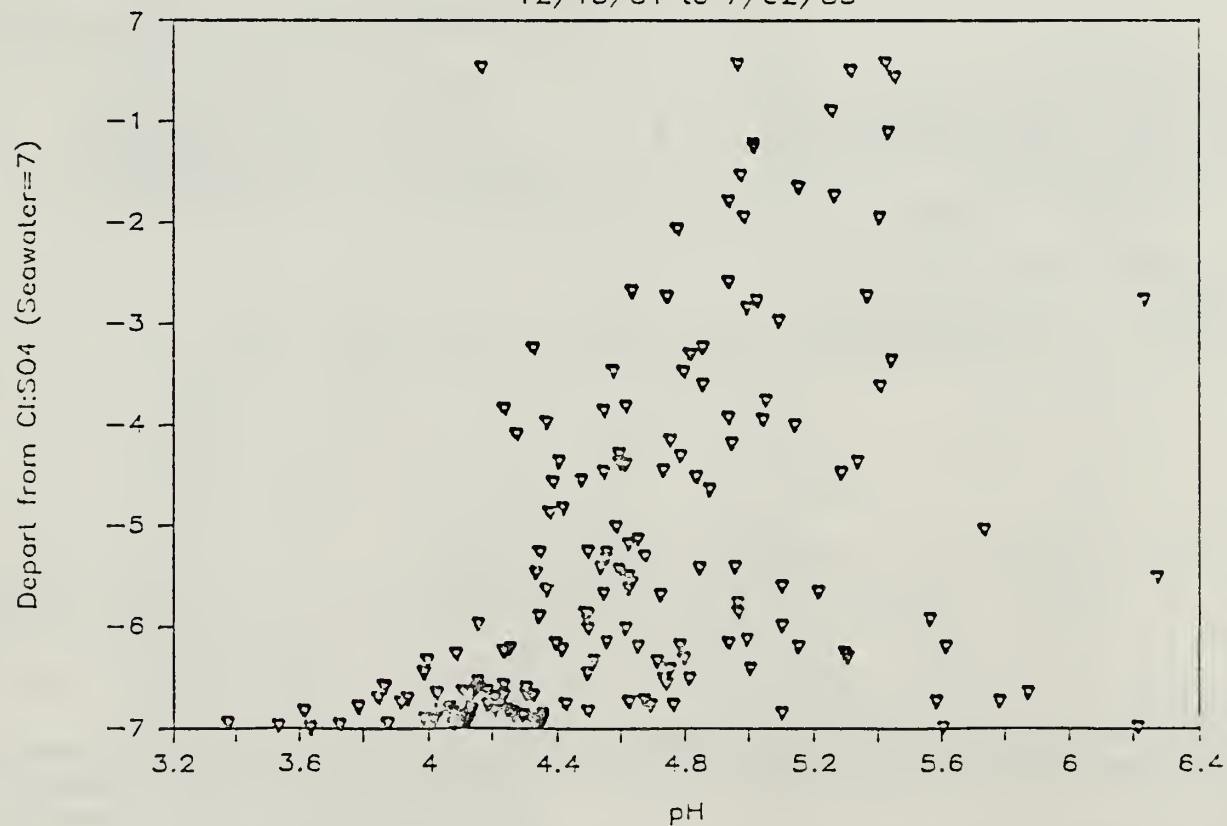


Fig. 5. Precipitation chemistry, Outer Cape Cod. A. Cl:SO<sub>4</sub> v Na:Cl  
B. Departure from Cl:SO<sub>4</sub> ratio of 7:1 v precipitation pH.



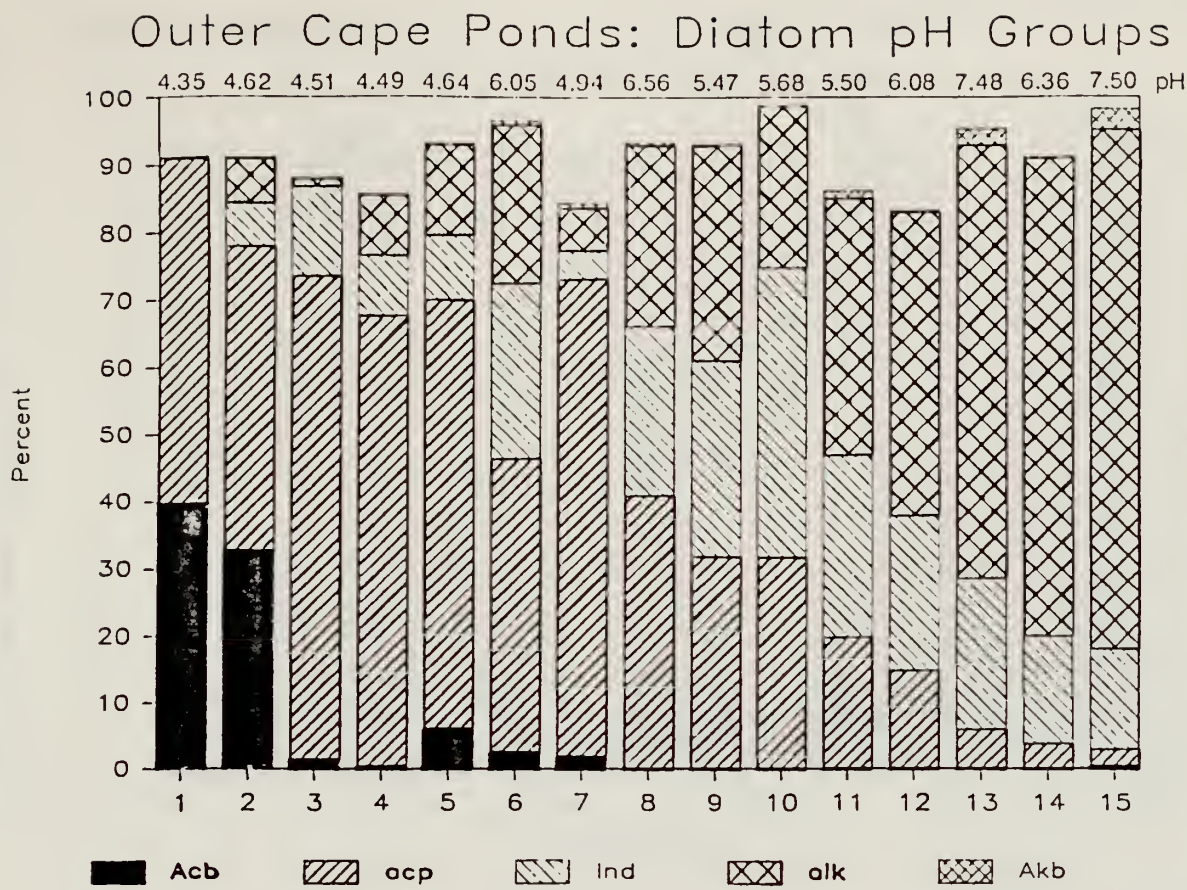


Fig. 6. Diatom pH Groups: Outer Cape Ponds. The pH value on this diagram is the mean pH calculated from all the measurements for each pond. Acb = Acidobionts, acp = acidophils, Ind = indifferent (circumneutral), alk = alkaliphils, Akb = Alkalibionts.

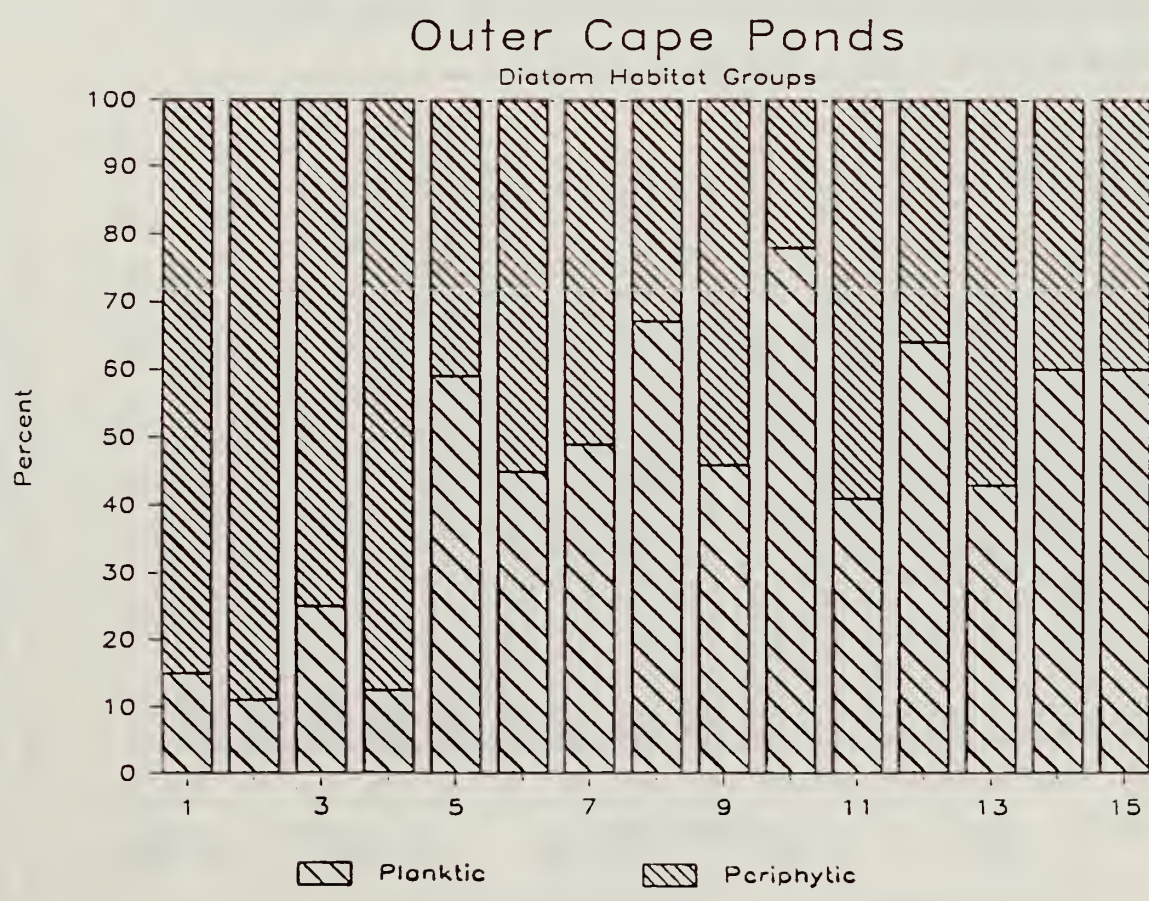
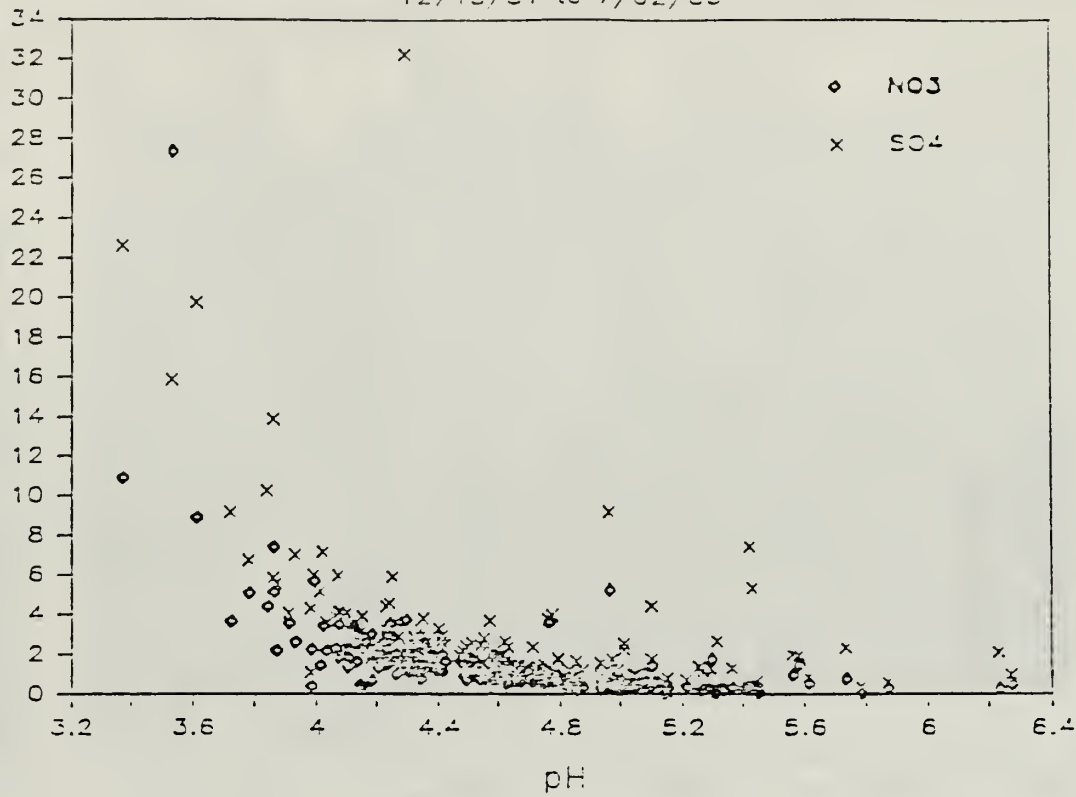


Fig. 7. Diatom Habitat Groups: Outer Cape Ponds.

PRECIPITATION CHEMISTRY: OUTER CAPE COD

12/15/81 to 7/02/85



Precipitation pH: Outer Cape Cod

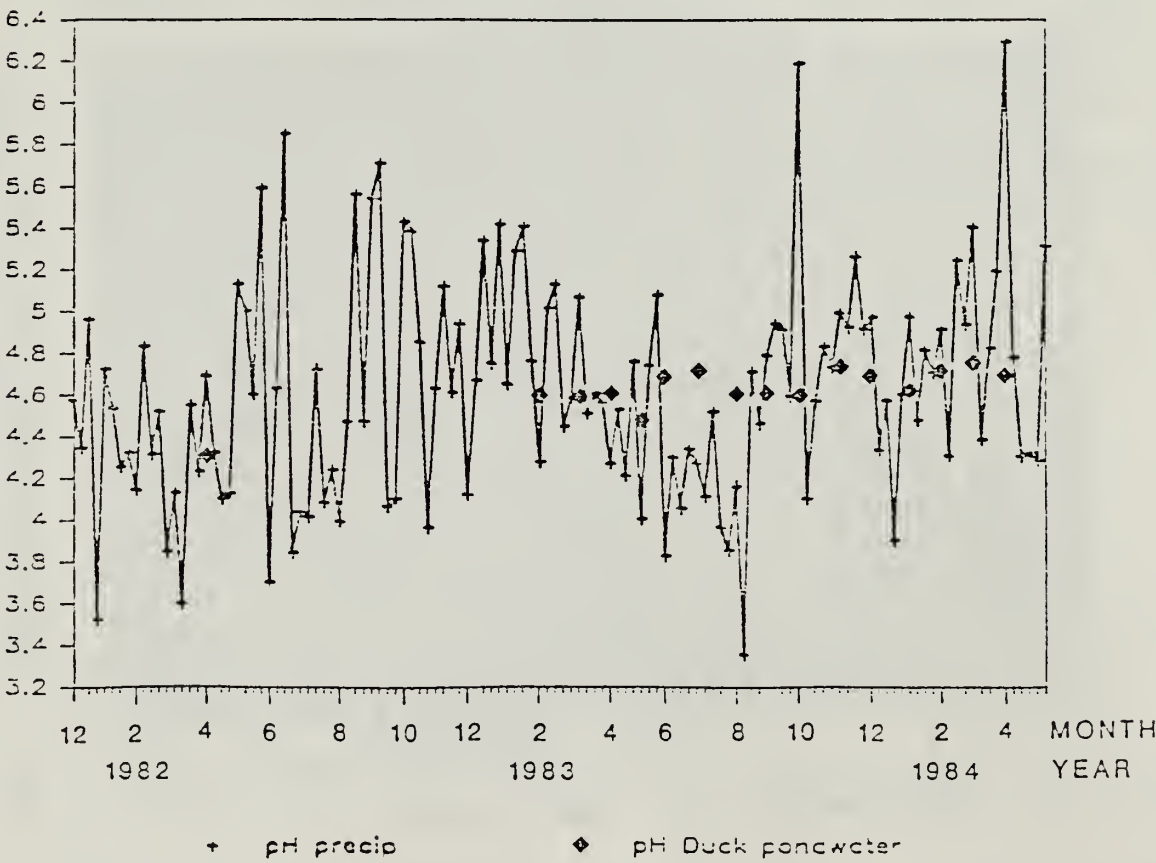


Fig. 8. Precipitation chemistry, Truro station, Outer Cape Cod. NO<sub>3</sub> + SO<sub>4</sub> v precipitation pH. Analysis done on a weekly basis by the NADP (National Acid Deposition Monitoring Program). Data provided by M. Foley and P. MacDonald, National Park Service, Boston

Fig. 9. Weekly readings of precipitation pH, Outer Cape Cod, for the period from 12/15/81 to 5/84. Observed pH values from Duck Pond, when taken during that time, are plotted on the same scale.



# DUCK POND, S. Wellfleet, Massachusetts

12,000-yr record: Diatom pH groups

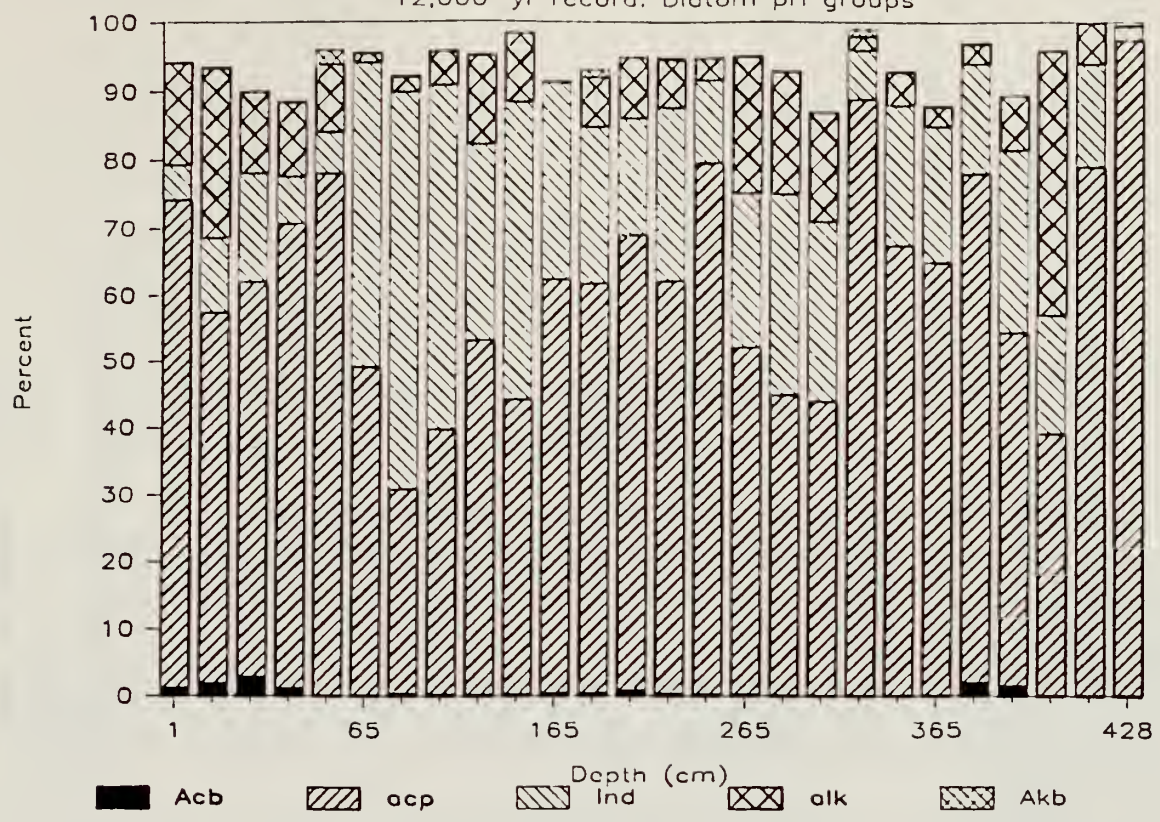


Fig. 10. Duck Pond Core D: Diatom pH groups.

## Duck Pond: Post-European Settlement

Diatom pH groups

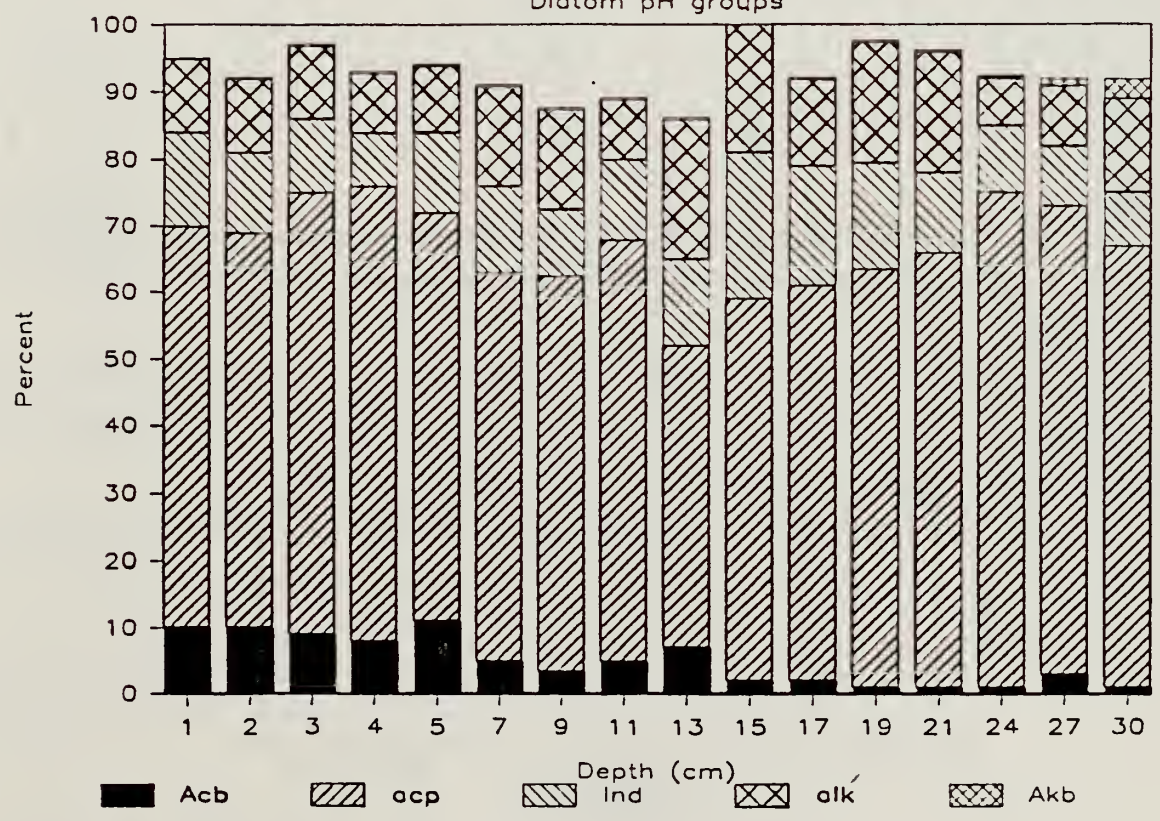
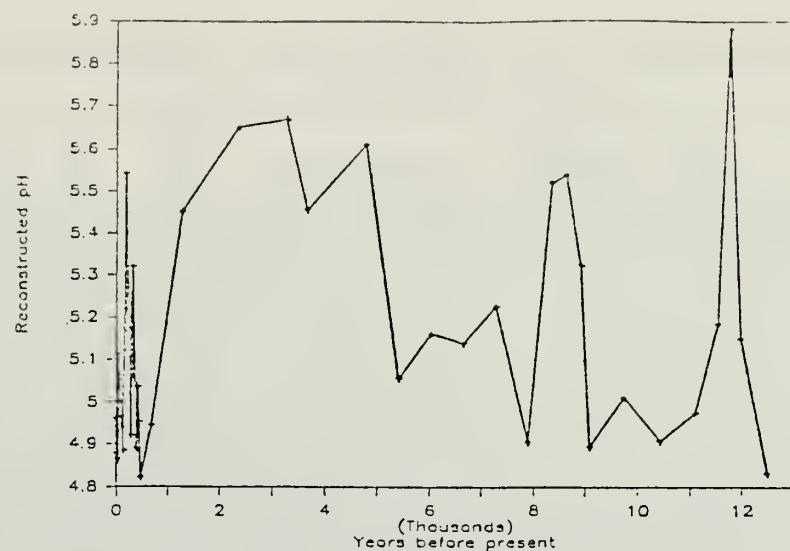
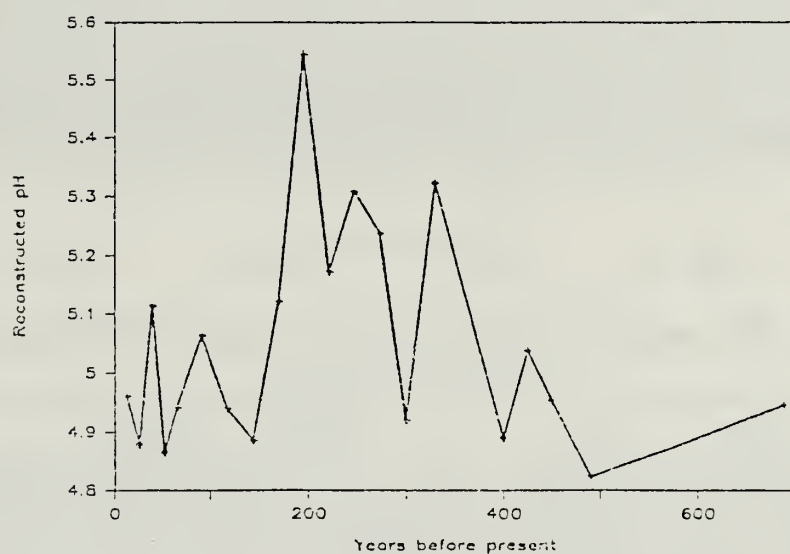


Fig. 11. Duck Pond post-European settlement core DD. Diatom pH groups. Acb = Acidobionts, acp = acidophils, Ind = indifferent (circum-neutral), alk = alkaliphils, Akb = Alkalibionts.



B Duck Pond, S. Wellfleet, Massachusetts



C Duck Pond, S. Wellfleet, Massachusetts

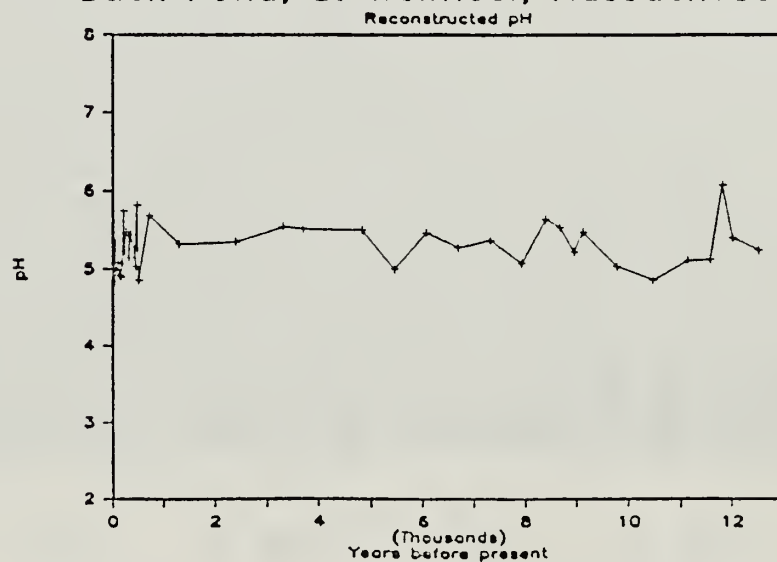


Fig. 12. Reconstructed pH of Duck Pond: Diatom-pH transfer function:

A. Core D, 12,000-year time series.

B. Core DD, 600 years to the present.

C. Both cores, 12,000-year series, expanded pH scale.



	Cao	Can	Fe	Na	Cl	ClA	Mg	Am	K	gulf	S
Kinnarum	4.00	0.80	15.00	4.10	4.35		14.00	3.00		89.00	86.00
Land	15.00	15.00	11.00	4.22	4.62	0.60			21.00	85.00	95.00
Dyer	11.00	4.80	25.00	4.25	4.51	0.60	6.40	3.00	30.00	86.00	94.00
Grease (W)	16.00	17.80	12.50	4.28	4.49	0.60	3.30	50.00	30.00	115.00	112.50
Duck	18.00	5.10	59.00	4.32	4.61	0.60	6.40	4.00	0.70	97.00	106.00
Grease (T)	11.00	7.00	45.00	5.80	6.03	1.20	14.00	7.00	0.80	130.00	127.00
Speckle	7.00	0.50	49.00	5.00	4.94		11.00	5.00		110.00	123.00
Gull	19.00	44.00	67.00	6.26	6.56	0.90	8.30	30.00	0.90	119.00	126.00
Thurbleach	5.00	10.00	46.00	5.46	5.47	1.80	8.20	5.00	0.50	146.00	143.00
Byder	11.00	8.30	78.00	5.45	5.63					113.00	120.00
Willams	2.00	3.60	41.00	5.00	5.50	1.20			0.50	122.00	99.00
Herring,W	4.00	8.10	64.00	5.80	6.08	6.80	27.00	6.00	0.90	119.00	120.50
Herring,E	11.00	17.90	49.00	6.39	7.49	3.70			50.00	517.00	741.00
Higgins	6.00	11.30	60.00	6.10	6.36	1.50	16.00	4.00	0.80	119.00	132.00
Pilgrim	2.00	146.00	60.00	7.50	7.50	8.00			2.20	946.00	
Kinnarum	0.80	0.80		11.00						3.20	
Land	1.59		12.00	12.90	21.20	1.50	1.59	3.00	1.00	225.00	6.29
Dyer	1.40	1.00	20.00	11.70	24.90	0.70	1.50	3.00	0.80	52.80	6.60
Grease (W)	1.50	1.10	12.00	15.40	32.00	0.90	2.00	0.70	1.00	294.80	
Duck	1.19	1.00	10.00	13.70	24.90	1.50	1.80	0.80	0.80	91.80	7.60
Grease (T)	5.29	1.80	37.00	16.90	35.50	1.70	1.80	0.80	0.80	77.00	6.15
Speckle	1.00	1.00		17.00						3.50	
Gull	1.90	1.50	10.00	17.10	32.00	1.50	2.99	0.10	1.09	396.00	9.20
Thurbleach	1.59	1.60	20.00	24.00		2.30	2.00	0.70	1.30	50.00	10.10
Byder										91.30	5.75
Willams	2.59		840.00	26.00	42.50	2.30	2.80	0.70	1.09	7.20	8.20
Herring,W	2.00	1.90	125.00	17.50	42.50	7.90	2.30	0.20	1.00	32.40	6.80
Herring,E	5.39	5.39	113.00	97.00	163.00	5.10	12.00	6.70	4.19	196.90	20.50
Higgins	1.59	1.70	35.00	17.50	33.50	1.90	2.39	0.50	1.09	67.80	7.50
Pilgrim	90.00	90.00	215.00	182.00	347.00	9.80	230.00	37.50	69.00	392.00	

Table 1. Morphometric and Chemical Data: Outer Cape Cod Ponds.

Mxd = maximum depth (m), ha = hectares, Plk = % plankton  
 diatoms, pho = 9/75 + 4/82 values, pha = mean pH (all values), P  
 = PO<sub>4</sub>-P, TP = total phosphorous, NN = Total nitrogen, nit =  
 NO<sub>3</sub>-N, Condo = conductance (umhos/cm), 9/75 + 4/82 values,  
 Conda = 1983 values, Alk = alkalinity, 4/82 values  
 (mgCaCO<sub>3</sub>/l), Cao = calcium, 1975, Can = calcium, 1983, Fe =  
 iron (ppb), Na = sodium (ppb), Cl = chloride (ppb), ClA =  
 chlorophyll a, Mg = magnesium (ppb), Amm = ammonia (NH<sub>4</sub>-N), K  
 = potassium (ppb), Voll = volume index calculated by multiplying  
 Mxd by ha, S = sulfate (ppb).

Mo/Yr	Temp	pH	Alk	Lang	Kinn	Long	Spec	Spec	Spec	Spec	Spec	Spec
	6	7	8	9	10	11	12	13	14	15	16	17
9/75	4.20	7.05	14.50	310.00	4.19	-1.50	97.00	5.00	-4.50	110.00	6.26	110.00
4/82	4.23	7.05	15.50	643.00	4.59	-0.30	93.00	5.99	1.30	122.00	6.40	113.00
2/83	4.37	7.13	15.40	643.00	4.59	-0.30	93.00	5.99	-0.10	104.00	6.03	117.00
3/83	4.50	7.13	17.10	751.00	4.60	-1.00	191.00	4.96	3.00	106.00	6.10	115.00
4/83	4.54	7.05	17.10	751.00	4.43	-2.10	114.00	4.32	-0.40	156.00	6.50	120.00
5/83	4.95	6.95	16.00	703.00	4.86		199.00	4.62		132.00	6.36	118.00
6/83	7.73	7.73	14.00	723.00	4.74	-1.10	104.00	4.77	-0.30	103.00	6.67	124.00
6/83	7.55	7.55	15.50	567.00	4.72	-1.00	194.00	1.75	-0.90	141.00	6.62	121.00
7/83	8.73	8.73	15.40	535.00	4.61	-0.30	110.00	4.72	-0.70	140.00	6.75	123.00
9/83	11.50	17.40	740.00	740.00	4.52	-1.10	195.00	4.21	-0.40	117.00	6.70	122.00
10/83	7.30	19.50	672.00	672.00	4.61	-0.30	109.00	4.59	-0.60	117.00	6.50	120.00
11/83	7.40	17.30	766.00	766.00	4.73	-0.10	193.00	4.92	-0.40	124.00	6.67	123.00
12/83	7.52	17.00	838.00	838.00	4.70	-0.20	110.00	5.02	-0.70	123.00	6.65	121.00
1/84	7.23	15.30	734.00	734.00	4.62	-1.20	197.00			122.00	6.12	121.00
2/84	7.34	17.00	730.00	730.00	4.72	-0.30	97.00	5.16	0.10	122.00	6.65	126.00
3/84	7.12	15.00	610.00	610.00	4.76	-0.70	109.00	5.15	0.20	100.00	6.60	123.00
4/84	7.26	16.30	843.00	843.00	4.70	-1.20	114.00	5.15	-0.40	131.00	6.55	126.00
5/84	7.41	16.07	740.75	740.75	4.61	-1.01	106.00	4.94	-0.27	123.23	6.51	125.00
Mean	6.39	10.20	610.00	610.00	4.19	-2.30	97.00	4.63	-4.50	100.00	5.69	115.00
Min Val	8.70	19.50	843.00	843.00	4.76	-0.10	104.50	5.15	3.80	156.00	6.26	136.00
Max Val	0.55	2.07	63.70	63.70	0.14	0.44	10.86	0.16	1.60	15.10	0.27	5.91

Mo/Yr	Temp	pH	Lang	Kinn	Long	Spec	Spec	Spec	Spec	Spec	Spec	Spec
	6	7	8	9	10	11	12	13	14	15	16	17
9/75	4.20	7.05	14.50	310.00	4.19	-1.50	97.00	5.00	1.30	110.00	6.26	110.00
4/82	4.23	7.05	15.50	643.00	4.59	-0.30	93.00	5.99	1.00	122.00	6.40	113.00
2/83	4.37	7.13	15.40	643.00	4.59	-0.30	93.00	5.99	1.00	104.00	6.03	117.00
3/83	4.50	7.13	17.10	751.00	4.60	-1.00	191.00	4.96	3.00	106.00	6.10	115.00
4/83	4.54	7.05	17.10	751.00	4.43	-2.10	114.00	4.32	-0.40	156.00	6.50	120.00
5/83	4.95	6.95	16.00	703.00	4.86		199.00	4.62		132.00	6.36	118.00
6/83	7.73	7.73	14.00	723.00	4.74	-1.10	104.00	4.77	-0.30	103.00	6.67	124.00
6/83	7.55	7.55	15.50	567.00	4.72	-1.00	194.00	1.75	-0.90	141.00	6.62	121.00
7/83	8.73	8.73	15.40	535.00	4.61	-0.30	110.00	4.72	-0.70	140.00	6.75	123.00
9/83	11.50	17.40	740.00	740.00	4.52	-1.10	195.00	4.21	-0.40	117.00	6.70	122.00
10/83	7.30	19.50	672.00	672.00	4.61	-0.30	109.00	4.59	-0.60	117.00	6.50	120.00
11/83	7.40	17.30	766.00	766.00	4.73	-0.10	193.00	4.92	-0.40	124.00	6.67	123.00
12/83	7.52	17.00	838.00	838.00	4.70	-0.20	110.00	5.02	-0.70	123.00	6.65	121.00
1/84	7.23	15.30	734.00	734.00	4.62	-1.20	197.00			122.00	6.12	121.00
2/84	7.34	17.00	730.00	730.00	4.72	-0.30	97.00	5.16	0.10	122.00	6.65	126.00
3/84	7.12	15.00	610.00	610.00	4.76	-0.70	109.00	5.15	0.20	100.00	6.60	123.00
4/84	7.26	16.30	843.00	843.00	4.70	-1.20	114.00	5.15	-0.40	131.00	6.55	126.00
5/84	7.41	16.07	740.75	740.75	4.61	-1.01	106.00	4.94	-0.27	123.23	6.51	125.00
Mean	6.39	10.20	610.00	610.00	4.19	-2.30	97.00	4.63	-4.50	100.00	5.69	115.00
Min Val	8.70	19.50	843.00	843.00	4.76	-0.10	104.50	5.15	3.80	156.00	6.26	136.00
Max Val	0.55	2.07	63.70	63.70	0.14	0.44	10.86	0.16	1.60	15.10	0.27	5.91

Table 2. pH, alkalinity, and conductance: values, means, and standard deviations for some of the Outer Cape Ponds. HE = Herring (Eastham), Duck = Duck Pond, Spec = Spectacle Pond, Gull = Gull Pond, Long = Long Pond, Kinn = Kinnacum Pond, Grel = Grel Pond

Table 3. Reconstructed pH history of Duck Pond, S. Wellfleet, Massachusetts. The mean pH (and standard deviation) of each pollen zone is calculated. The regression equation has an  $r^2$  of 0.89 and a standard error of the estimated pH of  $\pm 0.45$ .

<u>Time (yr B. P.)</u>	<u>Pollen Zone</u>	<u>mean pH (mlr w Akb)</u>	<u>mean pH (mlr w/o Akb)*</u>
150 - present	3e2	4.96 $\pm$ 0.08	4.95 $\pm$ 0.08
330 - 150	3e1	5.25 $\pm$ 0.17	5.23 $\pm$ 0.2
2200 - 330	3d	5.37 $\pm$ 0.43	5.02 $\pm$ 0.23
5000 - 2200	3c	5.6 $\pm$ 0.09	5.6 $\pm$ 0.09
8000 - 5000	3b	5.19 $\pm$ 0.23	5.1 $\pm$ 0.12
9000 - 8000	3a	5.46 $\pm$ 0.12	5.46 $\pm$ 0.12
10500 - 9000	2	4.97 $\pm$ 0.08	4.97 $\pm$ 0.08
11800 - 10500	1cb	5.41 $\pm$ 0.42	5.41 $\pm$ 0.42
before 12000	1a	4.83	4.83
 middle Holocene	 3a-3d	 5.38 $\pm$ 0.3	 5.24 $\pm$ 0.28
 150 - present	 3e2	 4.96 $\pm$ 0.08	 4.95 $\pm$ 0.08
12000 - 150		5.29 $\pm$ 0.29	5.2 $\pm$ 0.27
12000 - present	(overall mean)	5.23 $\pm$ 0.29	5.15 $\pm$ 0.27

\*This version of the equation was used in plotting Figures

Part I.

Technical Report

PREHISTORIC AND HISTORIC TRENDS IN ACIDITY OF THE OUTER CAPE PONDS

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## ABSTRACT

## PREHISTORIC AND HISTORIC TRENDS IN ACIDITY OF THE KETTLE PONDS IN THE CAPE COD NATIONAL SEASHORE

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Outer Cape kettle ponds are acid-sensitive ecosystems set in non-weathering crystalline outwash sands. They range in pH from 4.3 to 7.5. The acid ponds characteristically have negative alkalinities, low specific conductance, high nitrate values, and contain more than 70% acid and periphytic diatoms, while the alkaline ponds are subject to tidal influence. Pondwater pH has been relatively stable for the past two years although Cape precipitation pH has varied from pH 3.5 to pH 6.2 during the same time.

Diatoms in modern sediments from 15 ponds were divided into pH-related groups. Correlation analysis suggests that each pH-related group of diatoms reflects different characteristics of the ponds. Acidobiontic diatoms are inversely correlated with alkalinity while acidophilic and alkaliphilic diatoms are highly correlated with pH changes (but in different directions). Circumneutral diatoms are inversely correlated with % acid and % periphytic diatoms, while alkalibiontic diatoms are correlated with conductance and all the seawater-associated ions and reflect the coastal environment of the Cape.

Changes in pH over the past 12,000 years in Duck Pond were reconstructed through a transfer function. The reconstructed pH suggests that the pond has been acid for its entire history with a mean pH of  $5.2 \pm 0.3$ . High pH of 6 was caused briefly during the late-glacial by increased windiness and erosion. Although the diatom evidence indicates that Duck Pond did become more acid recently (with a mean pH of  $4.9 \pm 0.1$  for the past 150 years), the pH has varied both up and down throughout the Holocene, and Duck Pond has had acidity as low as the present at other times in the past 12,000 years. Significant correlation between charcoal influx and alkaline Fragilaria diatoms in the pre-European-settlement core and between % charcoal and total acid diatoms in the post-European-settlement core, highlight the effect of local alkaline inputs from forest fires in the drainage basin, in contrast to acidic inputs from windborne ash and gases from fossil fuel combustion. Inverse correlation between diploxylon Pinus species and reconstructed pH and linear correlation between haploxylon Pinus and alkaliphilic diatoms, suggest that vegetation changes reflecting climate and fire history, also affected the pH of the pond.

## BACKGROUND

The adverse environmental affects of toxic and acidic substances in precipitation have been recognized since the 1800's. Transport of acid-laden plumes of air from industrial areas to other regions has been documented by chemical analyses (Gorham 1957, 1961). Although it is believed that recent increases in acid precipitation have caused major problems in wetlands in sensitive regions of North America (Schofield, 1976, 1977; Davis et al., 1978; Hendrey et al. 1980; Canadian Embassy, 1982; Gorham et al., 1984) that are downwind of highly industrialized areas (Rahn and Lowenthal, 1985), the U. S. and Canada have only recently set up monitoring networks to analyze patterns and trends of toxic atmospheric pollution (Likens et al. 1979; Kahl et al. 1985)). Areas most affected by acid precipitation are the Adirondacks in New York, New England, and, increasingly, the southeastern and western states (Likens et al., 1979).

Rainwater has a natural pH of 5.6 (although recent studies indicate that unpolluted precipitation may have a wider natural range) (Galloway et al., 1984), but consistent annual values of as low as pH 4.2 have been measured in sensitive regions and acid precipitation events with pH of 2 or 3 have been monitored (Davies et al., 1984). Because of the continuous acid deposition, poorly buffered lakes in areas with non-calcareous crystalline rocks or those with abundant trace metals that can be weathered out of surrounding rocks (Al, Zn, Cu, Cd, Se) (Gorham, 1961; Herrmann and Baron, 1980; Cronan and Schofield, 1979; Grahn, 1980; Kahl et al., 1985, Charles, 1985) by acid rainwater, are believed to have become more acid and/or more contaminated with toxic trace metals. In certain lakes, this leads to changes in phytoplankton and zooplankton and to loss of amphibian and fish populations (Confer et al., 1983; Schindler et al., 1985). Many fish cannot reproduce in water with a pH lower than 5.6, although there are naturally-acid lakes with genetically-adapted

populations of acid-tolerant fish (Rahel and Magnuson, 1980).

In addition, acid and other toxic atmospheric deposition has injured and killed people (London smog, Belgium smog, Donora, Pennsylvania smog; Roueche', 1971) and destroyed forests and foodcrops (Braekke, 1976; Tamm, 1976; Galloway et al., 1978; Fabijanowski and Lesinski, 1980; Huttunen et al., 1980; Bennett, 1985) and buildings (limestone, marble, stained glass, paintings; Frenzel, 1985), as well as wetlands. It is an international problem and one in which the countries or regions producing the most pollution are, in many cases, separate from the countries and regions most affected by atmospheric deposition (Likens et al., 1979). As far as wetland ecosystem damage goes, acid degradation of lakes has been documented in Scotland and England (Davies et al., 1984; Flower and Batterbee, 1983), the Netherlands (van Dam et al., 1980), and Scandinavia (Almer et al., 1974; Wright, 1977; Wright et al., 1980; Henrickson, 1979; Renberg and Hellberg, 1982; Davis and Berge, 1980).

In the United States, although studies of sensitive regions are presently being conducted (PIRLA, 1985), few long-term lake pH histories have been completed (Ford, 1985). However, two experimental acidification projects are in progress in North America: a long-term project begun in 1975 on Lake 223 in the Experimental Lakes Area (ELA) in northern Ontario, Canada (Schindler et al., 1985), and a new study recently begun on Little Rock Lake in northcentral Wisconsin (Brezonik et al., 1986).

In North America there is documentation of increased nitrates and sulfates in the precipitation coming from air masses from industrialized areas (Galloway et al., 1984). But even though recent lake damage is indicated in some studies (Charles, 1984), the cause of some with-in lake changes such as the disappearance of fish, is not that clear (Ford, 1985, Kahl et al., 1985). Several questions must still be answered:

1. What lakes or sets of lakes have become acidified?

2. When did acidification of the individual lake system begin and what was the history and range of pH variation in the lake? This information cannot be elicited just by comparing the immediate pre- and post-European settlement changes. The disturbance history of the lake and the long-term pH trends, as well as evidence for naturally-occurring "reversals," must be determined.

3. What caused the acidification and what is meant by an acidified lake? Is this different from an acid-degraded lake?

4. When has acidity gone "too far?" Is this a question of our present use of/or need for the lake, or some point inherent to natural systems?

5. To what extent does low pH precipitation and acidic dryfall deposition affect lake pH?

6. What factors other than geology and soil make the relationship between precipitation pH and lake pH more "robust?" This involves knowledge of morphometry of the lake, the flushing rate of the lakewater (residence time), and the magnitude, direction, and timing (seasonality) of other impacts from various uses.

7. What can we do to solve the problem -- as a region, as a state, as a nation, or internationally?

These questions can be answered in two ways. Firstly, by a comparison of present-day chemical data with chemical analyses taken in the past, and secondly, by analysis of the continuous record of historical and prehistorical environmental change found in lake sediments. Unfortunately, there is very little reliable old chemical data (Likens et al., 1979; Haines et al., 1983, Kahl et al., 1985) and, in even recent efforts, there are important missing variables. In the 208 Water Quality Survey of Massachusetts lakes conducted in 1975 and 1976, no sulfate determinations were made and no minerology of the lakewater (no Al, Cd, etc.) was measured. Only in recent years has regional



lake monitoring been initiated and now chemical data from large numbers of lakes are being compiled (Poff, 1967, 1970; Winter, 1977; Gorham et al., 1983; Charles, 1982; 208 Survey, Mass., 1975).

On the other hand, lake sediment cores contain fossil assemblages which can be compared to arrays of modern assemblages and then correlated with modern chemical data. In this way inferences about the past can be made.

Algal fossils provide within lake information most relevant to lake acidification. In most lake environments, the frustules of diatoms (Bacillariophyta), algae with silica cell walls, are abundant and well-preserved. Diatoms have also been the object of much taxonomic and ecologic study (Hustedt, 1930, 1939; Huber-Pestalozzi, 1942; Nygaard, 1956; Foged, 1980; Merilainen, 1967; Round, 1961; Gasse, 1980, Gasse et al., 1983a, Gasse and Tekala, 1983b; Germain, 1981; Patrick and Reimer 1966, 1975; Patrick, 1977; Florin, 1980; Battarbee, 1979; Koppen, 1975, 1978; Charles, 1985a, 1985b; Camburn and Kingston, 1985; Lowe, 1974; PIRLA, 1985).

Diatom associations integrate pond pH. The accumulation of diatom frustules in the lake sediments represents the annual or decadal response of the biota in the lake. Seasonal and microhabitat variation are smoothed at medium frequency sampling intervals. Diatoms respond relatively rapidly to environmental changes such as pH, and also to salinity gradients and to changes in nutrient availability, water levels, and temperature (Hustedt, 1939; Patrick and Reimer, 1966; Patrick, 1977; Gasse, 1980). Diatoms are therefore reliable variables with which to reconstruct the environmental history of a lake, in general, and the pH changes within a lake, in particular. Correlation of chemical variables, morphometric factors, disturbance indicators, and pollen and diatom percentages, enable separation of some of the factors affecting diatom distribution from those caused by change in lakewater pH. Work on the taxonomy of other siliceous algal fossils

such as Chrysophyte cysts and Mallomonadacean scales (Nygaard, 1956; Smol et al., 1984) shows the promise of these fossils, also, as sensors of acidification changes within a lake.

Pollen analysis and radiocarbon dating of the sediments are necessary to provide a framework for diatom analysis of the lake cores. These techniques provide a history of regional vegetation and climate change and establish pre- and post- European-settlement boundaries and the timing of other well-defined pollen horizons. When choosing a site for diatom analysis, availability of modern chemical data is also crucial, as is an array of lakes in a similar geologic setting with a wider range of pH and other chemistry, so that all possible downcore variations in the history of the lake being studied will be taken into account.

## INTRODUCTION

Because of its geologic history and setting, Cape Cod, in southeastern Massachusetts, is one of the regions sensitive to the effects of acid deposition (Fig. 1). It has many kettle lakes set in non-calcareous, crystalline, coarse outwash sands (Strahler, 1966; Oldale, 1968) deposited about 17,000 to 14,000 years ago during the recession of the Laurentide ice sheet (Denton and Hughes, 1981) (Fig. 2). The ponds were formed by differential melting of stagnant ice blocks (Strahler, 1966; Winkler 1982, 1985a). Some of these freshwater kettle ponds are within the Cape Cod National Seashore (Fig. 1) and comprise a unique, diverse, and nationally important resource that should be carefully preserved. There is need for a definitive study of the prehistoric and historic acidity levels of the Seashore ponds because:

1. There is current concern for the effects of acid rain on poorly buffered kettle ponds.
2. There is preliminary evidence that some of the Seashore ponds have

always been extremely acid (Winkler, 1982).

3. The Commonwealth of Massachusetts wishes to initiate a program "treating" acid-degraded ponds with lime to raise the pH. This kind of treatment would result in degradation of naturally-acid lake ecosystems. Therefore, some knowledge of the natural variation of the pH within these ponds is necessary so that sensible management decisions can be made. Ponds that are naturally-acidified should be identified, as well as those undergoing anthropogenic acidification and/or toxification.

4. Very few long-term lake pH histories have been analyzed. However, the results from short-term histories of lake pH (covering the past 100 to 200 years) suggest that lake acidification is not synchronous, even within a region, and the causes of acidification and/or lake degradation are not that clear.

With these problems and goals in mind, I have reconstructed the 12,000-year pH history of Duck Pond in South Wellfleet, Massachusetts. I have used modern diatom assemblages and modern chemical data from lakes in the Cape Cod National Seashore in the Outer Cape (Eastham, Wellfleet, Truro, and Provincetown)(Fig. 1 and 2, Table 1), an area of about 36 km x 4 km in extent, to provide modern analogs in order to construct a transfer function for pH.

#### GEOLOGICAL SETTING, LIMNOLOGY AND MODERN CHEMISTRY: OUTER CAPE PONDS

Duck Pond (South Wellfleet, Massachusetts, 41°56'N, 70°00'W) is one of the many kettle lakes within the Wellfleet pitted outwash plain (Fig. 2) of coarse, crystalline sand (Oldale, 1968). It is an oligotrophic closed basin lake, about 5.1 ha in area, lying 2.5 m above mean sea level, with a maximum depth of 18.5 m and a mean depth of 5.9 m (Soukup, 1977) (Fig 3; Table 1). It presently has an average pH of 4.64 (Table 1).

The environmental history of Duck Pond is probably better known than any other pond on the Cape. It was the subject of a zooplankton study by MacCoy

(1958), and was the focus of a study of limnologic and land-use history of ponds in the Cape Cod National Seashore by Soukup (1977) which also provided some chemical and biologic data and important management recommendations for the Seashore ponds. A large amount of chemical information on some of the Cape Cod ponds was compiled in 1975 by the 208 Water Quality Survey (B. Peterson, pers. comm., 1983), by the more recent Acid Rain Monitoring project (ARM) (J. Portnoy and B. Samora, pers. comm., 1985), by the NADP Survey precipitation pH and ion analyses (National Park Service, M. Foley and P. MacDonald, 1985, pers. comm.), and by the Massachusetts Audubon Society study of Great and Ryder Ponds in Truro (E. Colburn, 1985 pers. comm.). Furthermore, the vegetation and climate history of the Outer Cape has been inferred from pollen, sediment, and charcoal analysis of a radiocarbon-dated sediment core from Duck Pond (Winkler, 1982, 1985a). A shorter core covering the time immediately before European settlement (about 330 years before 1980 on the Cape) until the present was also available for close interval sampling of the recent centuries.

The ponds on the Cape, although edaphically and geologically similar (Fig 2), fall within a broad range of pH values -- 4.09 to 8.3 (Fig. 4). The pH of 180 ponds was measured in September 1975 in a survey of Massachusetts ponds (208 Water Quality Survey, B. Peterson, pers. comm.). The pH frequency distribution appears tri-modal. It is evident from this data that most of the ponds on the Cape are acid with a pH between 5.2 and 6.7. There is also a group of very acid ponds in the pH range between 4.09 and 5.2 as well as another group of more alkaline ponds which have pH values between 6.76 and 8.3 (Fig 4). Although there is chemical data for each of these ponds, not much information is given about the sediments or nature of each pond in the survey. It is probable, though, that all of the high pH ponds are influenced by tidal seawater to some extent, while many of the low pH ponds are either



dystrophic bog ponds or oligotrophic ponds in crystalline outwash sands. The ponds within the modal pH range may have a long history of adjacent development and/or be set in the moraines of the Cape or in outwash derived from more nutrient-laden tills.

The 15 ponds chosen for diatom analysis of modern sediments on the Outer Cape generally represent a similar range of pH as the larger sample (Fig. 5), with pH values between 4.3 and 7.5. Seven of the ponds are within the 5.2 to 6.7 pH range, 2 are above, and 6 are below pH 5.

## METHODS

### FIELD

To obtain a set of modern sediment samples, Ekman dredge samples were collected on June 16th and 17th, 1983 from the deepest part of 14 ponds in the Cape Cod National Seashore (Fig. 1). The ponds were selected to represent a range of chemical parameters: pH, alkalinity, conductance, etc. as determined by water chemistry in past surveys (1975 Water Quality Survey, B. Peterson, pers. comm.; Soukup, 1977; J. Portnoy, pers. comm., 1982).

Earlier, in June, 1980, a dredge sample had been taken from Duck Pond in S. Wellfleet, Massachusetts (MAS-12, Winkler, 1982). At the same time, a 4.28 m core of lake sediments was collected from Duck Pond (D on Fig 3) using a modified Livingstone piston corer, 5 cm in diameter (Winkler, 1982) and a one meter core was obtained with a Davis-Doyle corer, 2 cm diameter (DD on Fig 3)). The longer core was taken from the deepest part of the basin under 18.2 m of water, while the shorter core was taken about 20 m northwest of the first core and in slightly shallower water (Fig 3).

### LABORATORY

The Duck Pond cores were subsampled in the laboratory and processed for pollen following methods described in Faegri and Iversen (1975) and Stockmarr (1971). The protocol for further sediment analyses is described in

Winkler (1985b) (Fig. 6). It includes subsampling and processing for charcoal analysis (Winkler, 1985c), loss-of-weight on ignition (Berglund, 1979), and carbonate analysis (Winkler 1985b).

The sediments from the Duck Pond cores, and also from the modern pond samples from the other Seashore lakes were prepared for diatom analysis by treatment with  $H_2O_2$  and potassium dichromate (van der Werff, 1955). Strewn mounts were than prepared according to procedures in Patrick and Reimer (1966). Permanent slides were made with Hyrax mountant, Refractive Index 1.7. The slides were counted under oil immersion at 1000 x magnification; a total of about 400 valves was counted for each level. Diatoms were identified using floras compiled by Hustedt (1930, 1939), Huber-Pestalozzi (1942), Patrick and Reimer (1966, 1975), Foged (1980), Florin (1980), Koppen (1975), Germain (1981), Gasse (1980), Gasse et al., (1983a), Gasse and Tekaiia (1983b); Camburn and Kingston (1985), and PIRLA (1985).

Radiocarbon dates were provided by the Radiocarbon Dating Laboratory of the Center for Climatic Research, University of Wisconsin-Madison. The dates are reported in Winkler 1982, 1985a, and by Bender et al., 1982.

#### TAXONOMIC COMPARISON

Because the diatom analyses of the Duck Pond sediments were done over a relatively large timespan (2years) and interest in the problem of acid depostion as reflected in the changes of diatom assemblages, had increased over this time, much new taxonomic information on diatoms from acid water systems has been generated (Ford, 1985; Charles, 1985; Camburn and Kingston, 1985; PIRLA, 1985). I was concerned that my taxonomic discrimination may have changed over time. To test the validity of counts made in 1983, comparison with more recent counts was made for diatoms in 3 Duck Pond surface samples. The frequency distribution of the major diatom taxa remained relatively the same in all the counts (Fig. 7).

## CHEMICAL DATA

Several sets of chemical analyses were used in this study. They are:

1. 208 Water Quality Survey of Cape Cod Ponds, provided by Bruce Peterson, Ecosystem Center, Marine Biological Laboratory, Woods Hole, Massachusetts (Fig. 8).

2. Morphometric and chemical data on several Seashore ponds, from Soukup (1977) (Fig. 8).

3. Determinations of pH, alkalinity, and conductance in several of the Cape Cod National Seashore Ponds, April 19, 1982, provided by John Portnoy of the Cape Cod National Seashore (Fig. 8).

4. Determinations of pH and several other chemistries (6/17/83), provided by Michael Soukup (National Park Service).

5. Acid Rain Monitoring Program chemical data on the Outer Cape Ponds from February, 1983 to May, 1984, provided by John Portnoy and Barbara Samora of the Cape Cod National Seashore.

6. Several 1984 analyses on Great Pond (Truro) and Ryder Pond (Truro) lake water provided by Elizabeth Colburn of the Massachusetts Audubon Society.

7. Sulfate determinations on some of the Outer Cape Ponds (9/14/84), provided by John Portnoy.

8. Ion and pH analysis of precipitation and dryfall deposition collected weekly within the boundaries of the Cape Cod National Seashore in Truro, Massachusetts. This data is part of the National Acid Deposition Monitoring Program (NADP) and was provided by Mary Foley and Patty MacDonald of the North Atlantic Regional Office of the National Park Service in Boston, Massachusetts. The period covered by this data was 12/81 to 7/85.

## FISH DATA

The data on fish populations in the Outer Cape ponds is scarce.

Joseph Bergin of the Division of Fisheries and Wildlife in Massachusetts provided the available information. It includes a survey done in 1911 of Gull and Higgins ponds and records from more recent rotenoning or seining and netting procedures used on Gull and Long ponds in Wellfleet and Great Pond in Truro. He also provided a history of liming treatments carried out on Great Pond (Truro), on November 5, 1973 and again in March of 1985. Williams Pond has also been limed on occasion (Soukup, 1977).

#### STATISTICAL ANALYSES

Analysis of this data was greatly facilitated by access to several programs written by Brian Goodman, of the Center for Climatic Research, University of Wisconsin-Madison, for the IBM-XT and AT microcomputers. These programs were used to calculate Pearson product-moment correlation matrices for chemical, morphometric, and biological variables, to generate multiple linear regression equations from the diatom and chemical data, and to plot stratigraphic arrays of diatom percentages from the raw counts. The correlation matrices enable separation of variables related to the pH changes within the pond from those related to other environmental factors.

Transfer functions (Webb and Clark, 1977) are used in paleoenvironmental analysis to reconstruct past variables from examination of spatial arrays of modern variables. Several transfer function equations for pH constructed by other diatomists concerned with acid systems were tested on the Outer Cape Pond data. Published equations based on Hustedt's pH groups (Hustedt, 1939) and indices derived from these groups (Nygaard, 1956; Renberg and Hellberg, 1982; Charles, 1985a), and equations derived from multiple linear regression of a select number of diatom taxa or the first principle component of this selected taxa (Davis and Anderson, 1984; Charles, 1985a), were fit to the Cape Cod data. Residuals for these equations showed skewed distributions. Some problems experienced when using weighted indices to



reconstruct pH of acid systems are discussed by Merilainen (1967), Renberg and Hellberg (1982), Ford (1985), and Charles (1985a). Besides, many of the regions for which equations were derived were not coastal, and consequently did not have a large range of alkaline lakes as well as acid ones. Because of the seawater influence on some of the Cape ponds and their evolutionary setting in non-calcareous outwash sands (representing two extremes of the pH scale), the Cape ponds have a wide range of pH values. I have generated a regression equation specifically for the Cape Cod data based on Hustedt (1939) diatom pH groups. The pH groups are:

Acidobionts (Acb): diatom taxa which optimally occur at pH values lower than 5.5.

Acidophils (acp): diatoms found primarily below pH 7.

Circumneutral (Indifferent) (Ind): diatoms occurring at or about pH 7.

Alkaliphils (alk): diatom taxa found primarily above pH 7.

Alkalibionts (Akb): diatoms which occur only above pH 7.

Assignment of diatoms into pH groups is also complex. Although many diatoms are found consistently in acid or alkaline lakes and placement of these species are clear, because of the geologic differences of regions, some species may be regionally dominant but not identified elsewhere (Charles, 1985b). Also, recent limnologic investigations may lead to change in the designation of some taxa and will certainly add to the knowledge of the ecology of diatom distribution (Charles, 1985a,b; Ford, 1985; PIRLA, 1985). With access to some of this recent information, I have used older literature designations combined with some new designations based on new work (Charles, 1985a) which seemed to fit with my experience with the diatom distribution within the Outer Cape ponds, to assign diatom species in my samples to pH groups (Appendix A).

I have used the equation based on these factors to reconstruct the pH history of Duck Pond.

## RESULTS AND DISCUSSION

### OUTER CAPE PONDS: MODERN SEDIMENTS

The modern diatom percentage data (Fig 9) from the Outer Cape Ponds generally show trends reflecting their present average pH (Fig 10). The distribution of Eunotia species (largely acid) and Fragilaria construens var venter (an alkaline form) expresses this relationship most strongly (Fig. 9). Frustulia, Tabellaria, and Neidium species appear to be present in high percents in only the more acid ponds, while Melosira (other than M. distans), Cyclotella comta, Fragilaria crotonensis and Asterionella formosa, Synedra, Navicula pupula and varieties, and Epiphytic diatoms (my combined title for Cymbella + Achnanthes + Amphora + Cocconeis + Gomphonema species) are found more frequently in the more alkaline ponds. Species of Pinnularia and Nitzschia appear in most of the ponds, while Cyclotella stelligera, Surirella, Fragilaria virescens var exigua, and Stauroneis are distributed in those within the modal pH range and are not found in the most acid, nor the most alkaline ponds (Fig 9).

It is surprising to note that most of the ponds, besides following the general trends noted above, have dominant diatom species which are, for the most part, unique from pond to pond. Kinnacum Pond, an acid bog pond, is dominated by Navicula subtilissima, Long Pond by Eunotia species, Great Pond (W) by a periphytic association of Eunotia, Pinnularia, and Frustulia, Duck Pond by Melosira distans and its varieties--with also relatively high percentages of Fragilaria construens var venter and F. brevistriata, both

Great (T) and Horseleech ponds by Fragilaria brevistriata and F. virescens var exigua, Spectacle Pond by Melosira liriata type diatoms, Gull Pond (one of the larger and deeper oligotrophic ponds) by high percentages of the planktic species Tabellaria fenestrata, and Ryder Pond by Cyclotella stelligera. Although there are these differences between the ponds in this small region, the distribution by pH group (Fig. 10), is very clear.

The ponds that have connections with tidal channels -- the Gull, Higgins, Herring, Williams complex in Wellfleet, Herring Pond in Eastham, and Pilgrim Lake in Provincetown (Fig 1) -- have abundant alkaline diatoms, with even some alkalibiontic forms. The other ponds have relatively few alkaline taxa, although ponds like Ryder and Spectacle have large circumneutral (Ind) diatom populations. The four most acid ponds (Kinnacum, Long, Dyer, and Great (W)), irrespective of morphometry (Fig. 8), water level, or trophic state (Kinnacum is a dystrophic bog pond and the 3 other ponds are clear, deep, and oligotrophic), have the highest percentages of periphytic (growing on or among aquatic plants) diatom types and very few planktic species (growing in the water column) (Fig. 11). A high periphytic/planktic diatom ratio in alkaline lakes may represent a drop in the water level of the lake and/or an increase in aquatic macrophytes in the broader littoral zone. Clearly, though, from the Outer Cape results, the meaning of this ratio in acid lakes is different and knowledge of pH history is important before inferences from a change in periphytic/planktic ratio can be made.

Examination of the morphometric and chemical characteristics of each lake (Fig. 8, Table 1), based mainly on values measured in 1975 and 1982, show that, as expected, the ponds with the most direct connection to the sea (Herring (E) and Pilgrim) have much higher conductance and higher amounts of Mg, Ca, K, Na, and Cl. These ponds, along with Gull-Higgins-Herring(W) ponds, have higher alkalinity as well. Great Pond (T) had high Ca at the time the

value was measured in 1975 (Fig 8) because it had been limed in 1973.

Subsequent measurement of calcium in Great Pond (T) was lower. Great Pond (T), the Gull chain of ponds, Horseleech Pond, and the alkaline ponds, all had high dissolved phosphate values. This may indicate the increased use and/or settlement around these ponds, since they all have very different morphometric characteristics. The acid oligotrophic ponds (Long, Dyer, and Great (W)) as well as the most alkaline ponds (Herring (E) and Pilgrim) have relatively higher ammonia and nitrate levels than the other ponds. Williams Pond had an unusually high iron content at the time of the measurement.

Additional chemical data became available for some sites since Fig 8 was drafted. The new values and the mean values of the variables such as pH, alkalinity, and specific conductance are presented in Table 2 and Figure 12. A correlation matrix of 31 variables including morphometric data (surface area (ha), maximum depth (m), and a volume index (VolI) made up by multiplying (ha) and (m), chemical data (old and new), and the diatom pH groups, are presented in Table 3.

The pH values are highly positively correlated ( $p = 0.005$ ) with surface area, conductance, alkalinity, P, Na, Cl, Ca, chlorophyll a, and the percentages of alkaliphilic, alkalibiontic, and planktic diatoms. The pH values are strongly inversely correlated ( $p = 0.005$ ) with the percentages of acidophilic, and total acidic diatoms, and with % of charcoal in the sediments. Morphometric characteristics of the ponds such as maximum depth and a volume index, were not correlated with any of the other variables, although the surface area (ha) was highly correlated with conductance, Ca, Na, Cl, Mg,  $\text{NH}_4$ , K, and the percent of alkalibiontic diatoms, as well as pH. I think that the correlation with surface area was dominated by the fact that two ponds with large surface areas (Herring (E) and Pilgrim) are alkaline and have tidal channels or seawater influence. The correlation of surface area



with the alkalibiontic diatoms indicates that the seawater relationship is a strong factor determining correlation, for there does not seem to be a significant relationship between morphometric factors and the more acid ponds. In the Outer Cape ponds, the older (1982) alkalinity values have a significant ( $p = 0.005$ ) linear correlation only with pH and none of the other chemical variables, and an inverse relationship with the percentage of acidobiontic diatoms. This evidence suggests that low alkalinity, as well as the low pH, is being sensed by the increase in percentages of acidobiontic diatoms in some of the modern samples from the ponds of the Outer Cape (Fig 10).

Among the variables most associated with acid deposition in the northeastern United States (Galloway et al., 1984),  $H^+$ ,  $NO_3^-$  and  $SO_4^{--}$ ,  $NO_3^-$  in the Outer Cape ponds is significantly ( $p = 0.01$ ) correlated with only one other variable, specific conductance.  $SO_4^{--}$ , on the other hand, is significantly ( $p = 0.005$ ) linearly correlated with specific conductance and all the ions that are identified with seawater,  $Ca^{++}$ ,  $Na^+$ ,  $Cl^-$ ,  $Mg^{++}$ , and with the % alkalibiontic diatoms which are also identified with the seawater influence on these ponds. Unfortunately, the only relatively complete set of values for  $NO_3^-$  that I had was from 1975, and the only  $SO_4^{--}$  values were measured in 1984.

The percentages of acidobiontic (Acb) diatoms were highly correlated ( $p = 0.005$ ) with the % of total acid diatoms and inversely correlated with alkalinity. The percentages of acidophilic (acp) diatoms were linearly correlated with the % of total acid diatoms and highly ( $p = 0.005$ ) inversely correlated with pH and the percentages of alkaliphilic (alk) diatoms and also inversely ( $p = 0.01$ ) related to the chemical variables,  $PO_4^{---}$  and chlorophyll a (both generally a measure of lake productivity). Percentages of circumneutral (indifferent) (Ind) diatoms are highly correlated with the total

percentages of plankton species and inversely correlated ( $p = 0.01$ ) with the percents of total acid diatoms in the samples. The percentages of alkaliphilic (alk) diatoms are highly ( $p = 0.005$ ) correlated with pH, conductance,  $\text{Na}^+$ ,  $\text{Cl}^-$ , new alkalinity values, and the % of alkalibiontic diatoms. They are also inversely correlated with the % acidophilic and total acidic diatoms. The % alkaliphilic diatoms are also correlated ( $p = 0.01$ ) with  $\text{PO}_4^{--}$  and chlorophyll a. The percentages of alkalibiontic diatoms (Akb) are highly correlated with total conductance, all the seawater-associated ions, and  $\text{NH}_4^+$ ,  $\text{K}^+$ , and  $\text{SO}_4^{--}$ .

These results suggest that each associated pH-diatom group may be reflecting different pond characteristics. The Acb group responds to low alkalinity, while the acp and the alk groups both strongly reflect pH changes (but in opposite directions). Interestingly, although the alk diatoms are correlated to productivity changes within the ponds, the acp diatoms are not correlated in any way with pond productivity changes. This partially supports the finding by Schindler et al., (1985) that in experimental acidification of Lake 223, productivity (as measured by chlorophyll a and plankton concentrations) did not generally decrease in the lake, even though phytoplankton and zooplankton species did change. Charles (1985a) also finds that in the Adirondack lakes, total P and chlorophyll a are not reflected in the diatom distribution.

There is a sharp decrease in total percentages of planktic diatoms in the more acid lakes of the Cape (Fig 11). A decrease in plankton diatoms and the concurrent increase in periphytic diatom species has also been noted in other acidic lake ecosystems (Norton et al., 1981; Renberg and Hellberg, 1982; Charles, 1985).

The Akb group closely reflects the coastal environment of the Cape and the influence of seawater -- either direct, or by windborne salt-spray -- on this

set of ponds. This characteristic makes this set of ponds unique among the groups of acid lakes that have been studied up to now.

The mean pH values and the diatom % pH distributions from 14 Cape ponds (Fig 10) (Duck Pond -- the pond for which the pH history was to be reconstructed -- was excluded from calculation of the regression equation) were used to construct a multiple linear regression equation which reconstructs the pH values of the ponds with an  $r^2$  of 0.89 and a standard error of the estimated pH of  $\pm 0.45$  (Table 4). Plots of the regression fit (Fig 13) and the residuals (Fig 14) from this equation show good correlation. A plot of the regression fit of several other equations from the studies discussed above (Fig 15) show that the unique factors influencing the diatom distribution in the ponds of the Outer Cape are not incorporated in the other equations although the pH trends are not that dissimilar.

#### DUCK POND: A 12000-YEAR DIATOM STRATIGRAPHY

Diatom percentages (Fig 16), pH groups (Fig 17), and diatom habitat types (Fig 18), can be examined along with the 12,000-year history of changing vegetation and climate of the Cape represented in the pollen diagram from the Duck Pond core (Fig 19). The pollen zones and the radiocarbon dates are placed on the diatom percentage diagram (Fig 16) to help intercompare the diagrams. The pollen zones were determined from major changes in the vegetation around Duck Pond as sensed by the changes in pollen percentages (Winkler, 1982, 1985a). The major vegetation changes are a function of the climatic changes during the 12,000 years of evolutionary history of Duck Pond (Table 5).

Major diatom assemblage changes (Fig. 16) for the most part correlate with the pollen zone changes. Before 12,000 yr B. P. (pollen zone 1a), an acidic

diatom assemblage dominated by Melosira distans is evident. This assemblage was found in sediments of the litter layer, vegetation growing around and in meltwater pools and on the soil covering the melting ice block that was to become Duck Pond. The acid water in these meltwater depressions was possibly caused by runoff over permafrost crystalline outwash deposits with some organic acid added from decomposition of the acid litter from the surrounding spruce-parkland vegetation (tundra and/or taiga). The landscape was very unstable during this time because ice blocks melted sometimes suddenly and sometimes slowly over thousands of years and collapse hollows and ponds, therefore, came into being at different times after deglaciation (Whiteside et al., 1980; Birks, 1980). As the landscape stabilized, but before the boreal forest association of spruce, jack pine, and green alder, became most abundant, a more alkaline diatom assemblage dominated the newly-formed Duck Pond. There were high percentages of several species of Diploneis, and also of Fragilaria construens var venter, F. brevistriata, Cyclotella comta, and C. stelligera. Somewhat similar diatom changes were found in a lake that has more recently formed from ice block collapse in outwash from the Klutlan glacier in the southwestern Yukon in Canada (Whiteside et al., 1980; Bradbury and Whiteside, 1980). In the Klutlan study, Diploneis species dominates during the time of stabilization of the vegetation around the new lake (Triangle Lake). The alkaline assemblage in Triangle Lake probably reflected an increase in conductivity in the lake (Bradbury and Whiteside, 1980) and possibly higher  $\text{Na}^+$  and/or  $\text{Cl}^-$  (Foged, 1953; Koivo and Ritchie, 1978). Lund (1959) also found a rather short-lived calcareous diatom assemblage in some lakes of the English Lake District during deglaciation. At Duck Pond, this Diploneis association of diatoms may have been the result of several factors:

1. a concentration of brines in summer meltwater seeping from areas



of buried ice (Gorham, 1961),

2. increased dustiness and long-distance transport of more nutrient-laden silts. Aerophilic diatoms (Hantzschia) are present in these sediments, or,

3. as the climate warmed and frozen ground surrounding the pond thawed, it is possible that most of the calcareous material that was in the outwash sands of the drainage basin leached into the pond at this time. This would especially be possible if there was increased seasonal precipitation falling on essentially unvegetated land.

By pollen zone 1b (11,800 - 11,300 yr B. P.), when boreal forest surrounded Duck Pond, there were very high green alder, spruce, and jack pine pollen percentages and the pond again had a dominant acid diatom flora. There were high percentages of Eunotia and Frustulia species and also a high percentage of Tabellaria and Epiphytic diatom species. These diatoms probably responded to an increase in nitrates fixed by alders surrounding the pond.

In pollen zone 2 (about 10,000 to 8200 yr B. P.) a deep pond is inferred. There are high percentages of the acid plankton diatoms Tabellaria and Melosira distans. The vegetation around the pond was dominated at first by a white pine and jack pine northern conifer forest and then by a white pine-pitch pine conifer forest. There were also high ericad (heath) pollen percentages. During the time of deposition of pollen zone 2 there was an extensive boggy margin of the pond, possibly increased acid runoff from decaying acid litter, and a warmer and wetter climate. There was also an increase in organic sediment influx into the pond (Winkler, 1985a).

Between about 9500 and 9000 yr B. P., as the climate became warmer and drier (pollen zone 3), pitch pine and oak increased around the pond and became the dominant vegetation on the Cape, as it is today, with the more mesophytic trees growing in protected moist hollows. By about 8200 yr B. P. (the

beginning of pollen zone 3b), charcoal abundances had increased and white pine had decreased. Because of an increase in local fires and inputs of the alkaline ash, a more alkaline diatom flora consisting of Cyclotella comta, Fragilaria construens var venter, the epiphytic diatom species, as well as Pinnularia species, was present in Duck Pond. From 8200 yr B. P. to about 2200 yr B. P., the major diatom species within the pond, Melosira distans and its varieties, vary inversely with Cyclotella comta and C. stelligera, just as the major components of the pine barrens vegetation in the region, pitch pine and oak, vary inversely during this time depending on the fire frequency (and, therefore, ultimately depending on the climate).

At the boundary of pollen zone 3d there are definite changes in the diatom assemblages. Both Cyclotella comta and C. stelligera decreased dramatically as Eunotia species increased. An increase in Melosira distans and Fragilaria virescens var exigua followed. Fragilaria virescens var exigua is one of the more acid tolerant Fragilaria species and this diatom assemblage probably reflects a period of increased acidification of the pond. There are concurrent increases in Myrica pollen and also in the pollen of herbaceous plants - notably Rumex and grass - which may indicate that there was disturbance of the land near the pond. Myrica is a nitrogen-fixing plant and increased erosion (organic and inorganic influx to the sediments increase at this time; Winkler, 1985a) would result in an increased flow of nitrate to the pond. The Eunotia bloom (and diversification) at this time might suggest a close relationship between Eunotia species and increased nitrates.

After European settlement on the Cape (about 330 years ago), marked by increased ragweed and herbaceous pollen and an initial decrease in pine pollen in zone 3e, further pronounced diatom changes are evident. Fragilaria construens var venter and F. brevistriata become abundant. Both of these alkaline diatoms respond to increased nutrient loading of the pond due to

forest clearance, increased erosion, and an increased influx of charcoal into the pond. There is also an increase in acidic diatoms -- Eunotia species, Asterionella ralfsii, Anomoneis serians var brachysira, and Tabellaria flocculosa. The reconstructed pH of the pond (Fig. 20) shows this well, with a slight rise in pH just after European settlement (a mean of  $5.23 \pm 0.2$  for the first about 150 years) and then a sharp drop in pH to a mean of  $4.95 \pm 0.1$  as windborne and local industrial acid gases and particulates were deposited. It was also at this time that the railroad stretched from Boston to Sandwich, a town on the Cape, and a reforestation program was initiated on the Outer Cape (Thoreau, 1849).

In an attempt to quantify some of the comparisons between the upland and wetland plant community changes, a correlation matrix containing both pollen and diatom species percentages and some of the other variables affecting lake environment (such as charcoal influx), was examined. There is significant linear correlation ( $p = 0.005$ ) (Table 6a) between the charcoal influx ( $\text{gm/cm}^2/\text{yr}$ ) and total Fragilaria species. An inverse correlation exists between the haploxylon pine (white pine) and the percent acidobiontic species, and an inverse correlation also is evident between diploxylon pine species (jack, red, or pitch pine) and the reconstructed pH. There is also a linear correlation ( $p = 0.005$ ) between the reconstructed pH and the percentage of alkaliphilic diatoms. Melosira distans is negatively correlated with the total percent of periphytic diatoms, and positively correlated with percent of acidophilic and total acidic diatoms. Surprisingly, Melosira distans is also negatively correlated with Tabellaria species, both of these diatoms being acid plankton species. This may indicate that these diatoms compete for similar nutrients or require different trace elements to become abundant.

Although charcoal influx is highly correlated ( $p = 0.005$ ) with total Fragilaria species (a generally alkaline group of planktic diatoms) in the

pre-European-settlement core (Table 6a), the % charcoal is highly correlated ( $p = 0.005$ ) with the percent of total acid diatoms in the post-European-settlement sediments (Table 6b). These results can be explained by the fact that while wood charcoal and ash deposited in runoff from local fires is generally alkaline, charcoal residues, windborne gases, and ash from fossil fuel burning are quite acid (Gorham, 1961; Davies et al., 1984). Most fossil fuel ash is windborne along with the acid gaseous components of fossil fuel combustion ( $\text{NO}_x$ ,  $\text{SO}_x$ , and  $\text{CO}_2$ ). The method used to analyze charcoal in the Duck Pond cores measures both wood and fossil fuel charcoal (Winkler, 1985b).

#### DUCK POND: DIATOM STRATIGRAPHY OF THE POST-EUROPEAN-SETTLEMENT CORE

In order to interpret the effects of post-European-settlement changes on the diatom stratigraphy with more certainty, contiguous sampling and analysis was done of another core from Duck Pond (DD, Fig 3). The diatom changes associated with pollen zone 3e, were essentially as reported above. Deposition time for the sediments analyzed was calculated using the rise in the percentage of Ambrosia (ragweed) pollen at about 24 cm in the core, to signify the European-settlement timeline (about 330 years ago) (Fig 21A). A constant deposition time was assumed for the remainder of the core and therefore a deposition time of about 13 years per cm was used to formulate a time scale. This fits well with the deposition time of 10.65 yrs/cm calculated for the same pollen zone in the longer core (Winkler, 1982, 1985a).

In this diatom percentage diagram (Fig 22) the most dramatic change takes place at about 12 cm in the core (about 150 years ago). There is an increase in Eunotia, and Melosira distans, while Melosira liriata and varieties, Fragilaria construens var venter, F. brevistriata, and Cyclotella stelligera



decrease. Although some diatoms such as Stenopterobia, Anomoneis serians v brachysira, and Surirella are present throughout the core, they increase slightly in abundance in the top 12 cm of the core and remain consistently elevated. Asterionella ralfsii and Eunotia exigua are present more consistently for the past 80 years, and Asterionella formosa appears about 50 years ago. Asterionella formosa is a dominant diatom in more eutrophic lakes and probably indicates (along with the increase in Melosira distans and varieties, and Tabellaria flocculosa) an increase in nutrients in Duck Pond most recently. There is a steady decrease in the percentage of total plankton species and a concurrent increase in the percentage of total periphytic diatoms (Fig 21B). It is obvious from the diatom pH group percentage diagram (Fig 23) that while most of the groups remained relatively constant during this time, the acidobiontic species increased, with the most dramatic increase happening since about 150 years ago. An increase in the alkaline and circumneutral (ind) diatom percentages (Fragilaria construens var venter, F. brevistriata, Cyclotella stelligera, Nitzschia, and epiphytic diatoms (mainly Achnanthes, Amphora, Gomphonema, and Cymbella)) is evident from shortly after European settlement (at 21 cm - about 270 years ago) to about 150 year ago and was probably associated with forest clearance. There was also an increase in Tabellaria species and a decrease in Fragilaria virescens var exigua from the time of early European settlement as well.

#### RECONSTRUCTED pH HISTORY OF DUCK POND

Reconstructed pH for this core (Fig 22,24) and for the two cores fit together (Fig 25A,B,C) shows that Duck Pond was acid for its entire history. The mean pH for the 12,000 years was  $5.2 \pm 0.3$  and it remained within a very narrow pH range (Fig 26A) although the climate and the vegetation changed

dramatically throughout that period of time. Reconstructed pH based on other equations (Fig 26B) shows that all the major changes discussed above would be interpreted from the use of any of them and also that the range of pH variation in Duck Pond has been small. There was a decrease in the pH of the pond in more recent centuries (Fig 24). From about 150 years ago the mean pH value was  $4.95 \pm 0.1$ , which contrasts with the mean pH of the remainder of the core of  $5.2 \pm 0.3$ . The pH was calculated two ways (Table 7). Firstly, using the entire set of pH groups including the alkalibiontic diatoms, and secondly, with the alkalibiontic diatoms set to zero. There are very few alkalibiontic diatoms in the Duck Pond sediments. The alkalibiontic diatoms that were encountered were very small forms from brackish or marine environments. I have plotted the reconstructed pH calculated without the alkalibiontic diatoms (Figs 20, 24, 25) on the assumption that these diatoms were windborne into the pond and do not represent a change in the ecology of the pond. The fact that the %Akb diatoms significantly correlate with the seawater ions in the modern samples (Table 3), and that the relative percents of the other diatom groups do not change when there are Akb diatoms in Duck Pond, persuades me that the assumption of "no change in pond ecology" is correct. However, the alkalibionts in the Duck Pond sediments (Figs 17 and 23) may very well signal increased windiness and possibly more frequent northeasterly storms during the Holocene (especially from 2200 to about 330 years ago).

When the mean reconstructed pH is calculated for each pollen zone (Table 7), it appears that there have been episodes of low pH at about 10,000 yr B. P., in the middle Holocene, and again about a millenia ago, as well as more recently (Fig 25B,C).

RECENT PRECIPITATION ANALYSES AND RECENT POND pH

Examination of the measurements of pH and ions in the rain and snow which fell weekly from December, 1981 to July, 1985 on the Outer Cape (NADP, 1985) clearly indicates that acid precipitation containing high amounts of  $\text{NO}_3^-$  and  $\text{SO}_4^{--}$  (Fig 27) is being continuously deposited on the Cape. The other ions in the precipitation are being deposited in the same proportion as they are found in mean sea water. For example, the Na:Cl ratio in seawater is about 0.61 (Gorham, 1961) and the Na:Cl ratio in precipitation on the Outer Cape is always approximately 0.61 (Fig 28A). However, the mean Cl: $\text{SO}_4$  ratio in seawater is 7:1, and it is clear from Fig 28A,B that the Cl: $\text{SO}_4$  ratio in the Cape precipitation is much lower. This evidence indicates that there is a large amount of  $\text{SO}_4^{--}$  ions from a source other than the sea being deposited on the Cape especially during very low pH precipitation events (Fig 28B). Furthermore, an "anion gap" (the lack of balance between the sum of cations (+) and anions (-)) strongly correlates with the very low pH precipitation (indicating the number of  $\text{H}^+$  ions needed to fill the gap) (Fig 29).

Surprisingly, though, comparison between recent monthly pondwater pH readings (Fig 12A,B, Table 2) and the precipitation pH (NADP, 1985) shows evidence of a trend towards increasing or stable recent pH for most of the ponds although the precipitation pH for the past 4 years was variable (Fig 30). Earlier lower pH values from Duck Pond: 4.19 and 4.32, were measured in September, 1975 and April, 1982, respectively. In fact, most of the Cape ponds had low pH readings at those times (Fig 12A,B). In a study of Cone Pond in New Hampshire, Ford (1985) noted that pH values taken in April, 1982 were much lower than any of her other measurements, were accompanied by high nitrates, and probably indicated a pH decrease caused by spring snowmelt. She

did not use them in calculating a mean pH value for the pond. It is possible that there was a series of very acid rain- or snow-falls in the northeast in the spring of 1982 which resulted in the low pH values in Cone Pond in New Hampshire and also in the low pH values in the Cape ponds. The mean precipitation pH for April, 1982 for the Outer Cape was low, about 4.43 (Fig 30), but more importantly, mean precipitation pH for March, 1982 was 4.15 and included very low pH rainfall (pH 3.5 and 3.85). This evidence suggests that the ponds may have been directly affected by acid rainfall in the spring of 1982 (snowmelt probably occurred by the end of February of that year because the mean March temperature in 1982 was above freezing (U. S. Climatology Divisional tapes of monthly temperature and precipitation data, 1931-1983, NOAA, Asheville, N. C.)). The seasonality of low pH rain may be an important factor in determining whether a pond will be able to buffer the acid inputs. In summer months, there are more alkaline inputs to the ponds due to increased use, and these buffer acid inputs from atmospheric deposition. There is no seasonal cycle to acid precipitation (Fig 31), but, up to now, there has been a seasonal cycle on the Cape which leads to increased nutrient loading of the ponds in summer (Soukup, 1977). Duck Pond did not have a low pH in June, July, or August of 1983 (Fig 12A), although the precipitation pH during that time was very low (Fig 30). Since March, 1982 had the lowest precipitation pH, seepage of this rainwater into the groundwater aquifer and into the pond through the soils of the drainage basin, with a lag of about a month, may have produced the low April, 1982 pondwater pH in Duck Pond (Fig 12A). The seepage component of precipitation may be as important as direct precipitation upon the pond. The area of the drainage basin of each pond is therefore important when calculating the effects of acid deposition. Some buffering takes place in the soil before the rain percolates into the groundwater, but the amount depends on the vegetation and soils of the catchment. There are pitch pine



forests and ericad heaths surrounding many of the ponds on the Cape and the generally acid soils of the Cape (podzols and peats) derived from this acid plant litter and the crystalline outwash sands, do not have much buffering capacity.

There is, additionally, increased nitrate and sulfate in the dryfall that is being monitored on the Outer Cape (NADP, 1985). Therefore, acid and toxic particulates are constantly being deposited in the Cape environment. Possibly, after a period of drought, one storm may wash the concentrated particles into the pond, leading to a sudden pH drop similar to low pH values noticed in streams and rivers during snowmelt (Kahl et al., 1985; Davies et al., 1984). However, if the storm originated in the northeast, it would have abundant seawater ions which would aid in buffering the effect of a sudden inwash of acidic ions. There must be a strong directional component to the acid deposition, with the predominant flow of southwesterlies bringing industrialized air to the Cape (Rahn and Lowenthal, 1985) and the occasional northeasters adding a good dose of seawater ions. Of course local circulation patterns such as winds which accompany tidal flows, and morning and/or evening fogs caused by the difference in the rate of temperature change over the land and the sea, contribute seawater ions to the Cape environment on a daily basis.

## CONCLUSIONS

### IMPLICATIONS OF DUCK POND pH HISTORY

The reconstructed history of pH of Duck Pond provides interesting insights for the recent discussion of the effect of acid precipitation on the Outer Cape ponds. Although this study should be considered primarily as the history of one pond, it is possible, because of the similar edaphic settings of other

ponds on the Cape, that inferences made from the Duck Pond data may apply to other outwash kettle ponds on the Cape.

Duck Pond was an acid pond throughout its 12,000-year history. It had a pH of about  $5.2 \pm 0.3$  throughout this time. While the pond has become more acid in the past 150 years (with a mean pH of  $4.95 \pm 0.1$ ), periods of as low pH in the past were also common (Figs 20,24A,B,25B,C)). The most alkaline (but probably never much above pH of 6) interval in the evolution of Duck Pond took place immediately after deglaciation and probably resulted from increased windiness and increased erosion of sparsely vegetated soil. Several other alkaline episodes were evident in the middle Holocene (during the period from 8000 to about 2000 years ago) and may have been caused by lower lake levels and increased input of charcoal from more frequent local fires.

The more acid periods in the history of Duck Pond were caused by a combination of the soil (crystalline sand: non-calcareous, non-weathering) and the vegetation (continuous cover of coniferous forest: spruce, fir, and jack pine, jack pine-white pine, white pine-pitch pine, and pitch pine, with many ericaceous shrubs -- all providing acid litter) surrounding the pond, in addition to atmospheric inputs. Acid or toxic atmospheric inputs if continuous and abundant, will add to the balance of the soil and vegetation inputs and will cause increased toxification of the pond. Volcanic ash is highly acid and may have contributed to the low pH at about 6000 yr B. P. (Mt. Mazama, in Oregon, erupted at this time) and at other times. Forest fires in the Midwest (although ash remaining on the ground from a wood fire is alkaline, there is an acid component to the gases) and on the south Atlantic coastal plain may have broadcast acid gases in air masses traveling over the Cape. Increased  $\text{CO}_2$  in the atmosphere, possibly from volcanic eruptions, or increased temperatures which would increase the  $\text{CO}_2$  exchange from the sea surface into the air, may have provided increased acidic components in the

atmosphere. Changes in atmospheric CO<sub>2</sub> during the Holocene are not well known although the analysis of gases trapped in bubbles in some of the ice cores suggest that there were fluctuations in CO<sub>2</sub> at times in the past (Neftel et al., 1982; Berger et al., 1985).

The cause of the most recent acidification of the pond is clear and stems from atmospheric inputs from industrial centers off the Cape and land-use changes on the Cape. By the mid-1800's, coal was being used in factories in the mid-Atlantic and New England states, and a railroad reached to Sandwich by the 1840's (Thoreau, 1849) and soon stretched the length of the Cape. The old railroad bed is now a powerline corridor and runs close by Duck Pond and several of the other ponds. Also by the 1840's, the demand for fuel by local industries such as glass-making and whale-oil rendering, as well as the need for heat and houses and roads (early Provincetown streets were made from wood) had already cleared the Cape of most trees (Jorgensen, 1978). Reforestation was started in the 1840's to restabilize the sandy soil.

The Cape has a special climate. The influence of the sea provides mild winters and mild summers, but it also provides frequent particulate-laden fogs. These fogs "burn-off" early in the day most of the time, which means the particulate matter in the fog droplets is deposited daily on the surrounding vegetation, soil, and surface of the freshwater ponds. Many of the ions in the fog droplets are in proportion with those in seawater, similar to the Na:Cl content of the precipitation (Fig 28). But, with increased seasonal traffic, these fogs often incorporate the nitrous oxides from automobile exhaust, and deliver them daily to the environment. The increased nitrates in the acid ponds may be caused by this element of Cape ecology in addition to the increased nitrates from more extra-regional sources. It is important to monitor these kinds of local inputs because it has been found that there is ozone damage to vegetation — on land and probably within

freshwater as well -- which is caused by phototoxic reactions in the presence of high nitrates (Abelson, 1985; Bennett, 1985).

Although Duck Pond is an acid pond and responds to acid deposition, it has been able to balance pH variations during its history. If adequate limits are put on industrial toxic and acid emissions, the pond will survive recent acid deposition because it has increased, as well as decreased, in pH before. It responds fairly rapidly to changes in inputs (possibly in weeks or months) and probably has a rapid flushing rate.

Other investigators have found that evidence of acidification and the timing of acidification of ponds is varied. From analysis of recent chemistry from ponds, rivers, and streams in northeastern Maine, Kahl et al. (1985) found that only one pond (at a high elevation) had gotten more acid recently and there was evidence that this pond had been acid for at least 200 years. Ford (1985) concluded that Cone Pond, in New Hampshire, had a long presettlement history as an acid pond. Battarbee (1984) has found much variation in the pH history of lakes in Scandanavia, Britain, and Europe -- some becoming acid-degraded in past decades, and some showing acid degradation about 150 years ago. Pennington (1984) documented the history of naturally-acid lakes in England and found that some became increasingly acid 5000 yrs B. P. partly because of a wetter climate.

Because everything travels downhill, it is easy to see why acid deposition has been considered a lake ecosystem problem. But, as stated in the introduction, polluted atmospheric deposition affects other ecosystems as well. "Treating" a lake does not cure the problem and furthermore, may imbalance the lake ecosystem and cause eutrophication. Unless there is more control over atmospheric inputs, there is no adequate treatment. Liming or filtering must be done in the smokestack, not in the lake, if it is to have a beneficial, long-term effect.



Major conclusions from this study:

1. Duck Pond, and the other acid ponds of the Outer Cape, are extremely sensitive to local and atmospheric inputs because of their geologic and edaphic setting. All the ponds in the Outer Cape which do not have tidal influence have very low specific conductance (less than 100 umhos/cm, Figs 8,12; Tables 1,2). Most ion deposition in the ponds comes from the atmosphere and includes abundant seawater ions (Fig 28).

2. Definite characteristics can be described for the acid lakes on the Outer Cape. They all have high percentages of acidobiontic and acidophilic diatoms (higher than 70% total acid diatoms) (Fig 10), more than 75% periphytic diatoms (composed mainly of acid species of Eunotia, Frustulia, Pinnularia, and Navicula) (Fig 11), high nitrate levels, low specific conductance, and negative alkalinity values (Fig 8). These similarities exist even though the morphometry and trophic state (dystrophic, oligotrophic) of these ponds differ.

3. Although there is definite documentation of acid precipitation on the Cape (Figs 27,30), and of low pH in the ponds (Table 1), especially in the early 1980's, recent pond pH values have been relatively stable (Fig 12; Table 2).

4. Duck Pond has a 12,000-year history as an acid lake ecosystem with a mean pH of  $5.2 \pm 0.3$  (Fig 20,23,25A,B,C,Table 7).

5. Since about 150 years ago, the pH of the pond has dropped from the mean pH value of  $5.2 \pm 0.3$  about 0.3 pH units to a mean pH of  $4.95 \pm 0.1$  (Fig 24, Table 7).

6. The pond has had pH variations in the past due to vegetation, and temperature and/or water level changes. Also, atmospheric loading of acid or alkaline dust, charcoal, and gases from volcanos and forest fires, and changes in atmospheric CO<sub>2</sub> in the past, may have affected the pond over a longer

period of time.

7. Duck Pond appears to be able to balance (buffer in some way) acid loadings because it has increased as well as decreased in pH in the past. The continuous salt spray from the ocean may aid in buffering, but also adds acid anions like  $\text{SO}_4^{--}$  and  $\text{Cl}^-$ . Duck Pond probably does not have high amounts of toxic trace metals in the drainage basin (such as aluminum) which would, on one hand, buffer increasing acidity, but, on the other hand, is, in itself, toxic to the biota in freshwater ecosystems. (This has to be tested, but there is some negative evidence for this hypothesis. No Fragilaria acidobiontica diatoms have been found in the Duck Pond sediments nor in the modern sediments from the acid Cape ponds. This diatom has been recently identified as an acid water (pH below 5) indicator species in aluminum-enriched lakes in the Adirondacks and New England (Charles, 1985b; Ford, 1985).

8. There may be a seasonality factor determining the affect of acid deposition on the Seashore ponds. When low pH rain is deposited in spring, winter, or fall, the effect of the acid loading (either by direct deposition or from seepage through the soils of the drainage basin) may be enhanced. If low pH rain comes immediately before or coincident with summer nutrient additions within the watershed, the effect of the acid on the pond is buffered (Fig 30). This would not be the case with deposition of toxic trace metals or other toxic substances -- some of them from local as well as extraregional sources -- which remain for a long time in the sediments of the lake. High lead levels measured in 1984 in Ryder Pond (Colburn, 1984, pers. comm.) probably are the result of wash-in from automobile exhaust from the adjacent highway (Fig 1).

9. Great Pond (T), which had been limed in 1973, had a pH of 6.3 in 1975, when the other acid ponds were relatively lower, but Great Pond (T)

subsequently reached a pH of about 6.3 again in recent years without further liming. Although  $\text{Ca}^{++}$  values increased after the liming in 1973, the alkalinity (generally an indication of the buffering capacity of a lake) stayed relatively constant (Fig 12).

10. The Outer Cape ponds have lakewater chemistry that is unique from pond to pond and the chemical characteristics of the aquifer is closely sensed by the diatom assemblages in the modern sediment samples from these ponds. However, this fact does not obscure the relationship between pH and the diatom pH groupings. Because the ponds exchange water with the ground, it is important to determine if these chemical differences represent aquifer differences and were always present or if they were caused more recently by settlement or development changes.

11. Diatoms are very sensitive indicators of the pH and pollution status of freshwater ponds and should be monitored on a regular basis -- possibly every other year or every five years -- especially since major development changes are occurring in the region.

12. The timing of acidification of ponds in the Northern Hemisphere is not synchronous (Battarbee, 1984; Ford, 1985). Present industrial emissions can increase acid in naturally-acid ponds, but probably does not cause it. However, degradation of lake ecosystems can be caused by the increase of toxic metals released through acid weathering of soils and rocks, and by toxic chemicals (PCBs, PAHs, etc.) also found in industrial emissions (Tan and Heit, 1981) as well as from acid deposition.

13. Although there is acid deposition into the Outer Cape ponds, this problem does not require immediate action such as chemical manipulation. Large-scale manipulation such as liming may actually tip the balance in these delicate ecosystems and lead to problems of lake eutrophication. However, sensible environmental policies should be adopted and enforced right away by

federal, as well as local governments. These policies must include strict industrial and automobile emission controls at the federal level, and, at the local level, zoning controls to limit erosion and prevent over-pumping and contamination of the Cape freshwater aquifer, to provide safe guidelines for sewerage disposal, and to initiate continuous monitoring of groundwater and pondwater chemistry and of pond biology. If this is done, Duck Pond, and the other Outer Cape kettle ponds, will remain important, unique, and evolving ecosystems.

#### MANAGEMENT RECOMMENDATIONS

1. There is no immediate threat from atmospheric acid deposition to the kettle ponds of the Cape Cod National Seashore. Most of these ponds have been acid ecosystems for their entire evolutionary history. However, there may very well be more local problems caused by increased use of the ponds and the rapid recent development of the Outer Cape. Increased demand for freshwater and increased amounts of groundwater pollution will lead to lowering of water quantity and quality in the ponds. Increased traffic, combined with the unique ocean-related climate characteristics of the Outer Cape (including abundant or daily fogs) may provide toxic levels of  $\text{NO}_x$ , Pb, and other toxic elements to the ponds and the vegetation surrounding the ponds. The fog aerosols should be analyzed to determine if there are seasonal chemical changes and how these affect the Cape ecology. Monitoring diatom assemblages in the ponds already sampled would enable the Seashore to identify change, to determine the direction of change, and to measure the rate of change caused by some of these factors. By monitoring the diatoms and the chemistry of the ponds on a regular basis, a natural experiment could be conducted on these acid ponds which would yield valuable information about naturally-acid lake



ecosystems.

2. In addition, because any kind of toxic atmospheric deposition is usually not a local problem, sensible local, regional, federal, and international policies to limit toxic emissions and to monitor pollution effects should be initiated as soon as possible. They should include:

- a. liming of smokestacks (not ponds), using scrubbers and filters, or whatever is necessary to limit polluting emissions.
- b. the monitoring and testing of emissions for toxic compounds other than acid substances,
- c. a decrease in auto emissions (including  $\text{NO}_x$ , Pb),
- d. groundwater testing and limits on pumping of freshwater
- e. erosion control and sewage disposal controls
- f. no experimentation on Seashore ponds unless ecological history is known and experimental affects can be reasonably predicted.

3. The ecology of the acid Outer Cape ponds is unique. Within the memory of anyone living on the Cape today, the ponds have not been fish ponds. They should be maintained as swimming and boating ponds, because ocean fishing facilities on the Cape are abundant.

#### RECOMMENDATIONS FOR FURTHER WORK

1. A study of the pH history of Great Pond (T) from diatom analysis should be done. Because the pond was limed in 1973 and again in 1985, two recent timelines would be demarcated. Also, since the pond is so close to Route 6, the major highway on the Outer Cape, another time interval coinciding with the construction of this road would probably be evident in the sediments.

2. Diatom analysis of sediments from Gull Pond would provide information about the timing of separation of the ponds in the Gull-Higgins-Herring

complex as well as a pH history. The presence of marine diatoms in the sediments may correlate with sea level-rise or increased storminess during the Holocene in the region.

3. Diatom analysis of the sediments of another of the acid ponds (Long, Dyer, or Great (W) will test whether the results from the Duck Pond reconstruction are unique to this pond or have broader application. The equation that has already been generated can be applied to the results from any of the above studies.

4. Mineral and ion analysis (especially Al, Cd, Se, Zn, Cu, Pb, as well as  $\text{NO}_3^-$  and  $\text{SO}_4^{--}$ ) of:

- a. modern sediments from the lakes,
- b. downcore sediments from Duck Pond,
- c. groundwater from wells near the ponds,
- d. and fog aerosols.

5. Expand modern sediment sample array

- a. this may provide a closer fit of the reconstruction equation
- b. when a larger number of sites are used, the number of variables used in generating the regression equation can be expanded.

6. Diatoms are sensitive to changes in acidification and eutrophication. Monitoring diatom assemblages in the ponds already sampled would enable the Seashore to identify change and the direction of change and to measure the rate of change. In other words, by simply monitoring the diatoms and the chemistry of the ponds regularly, a natural experiment could be conducted on these acid ponds.

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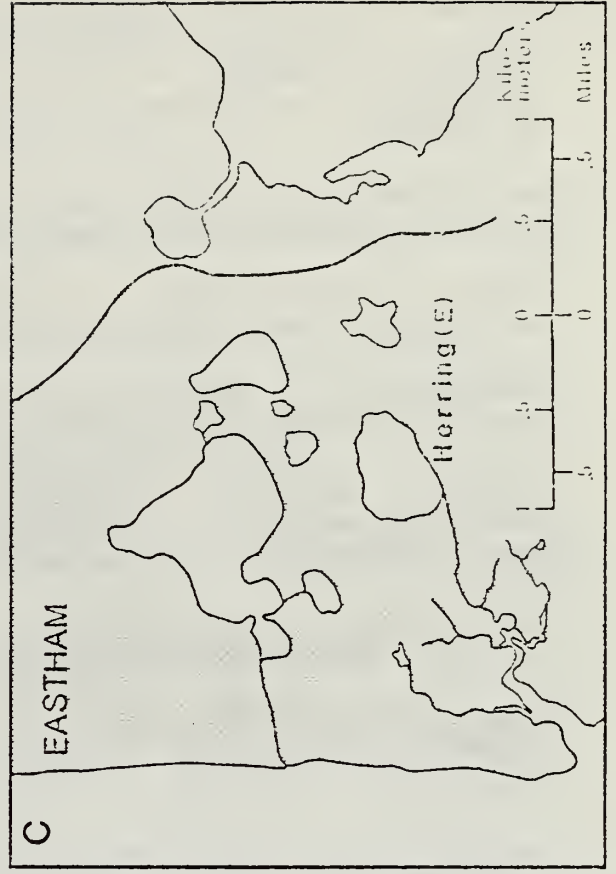
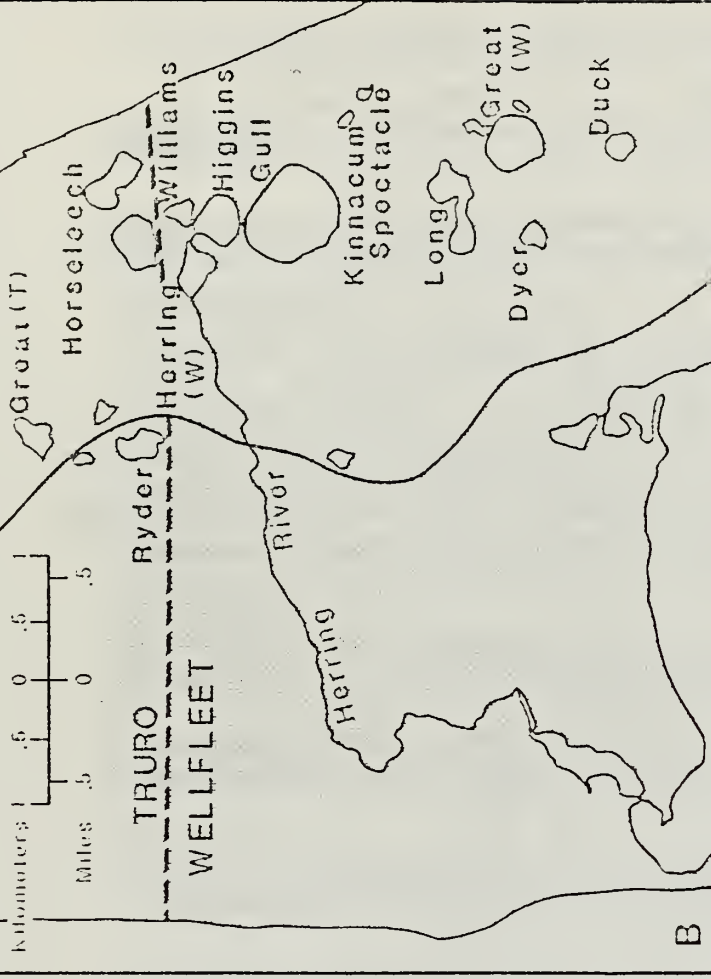
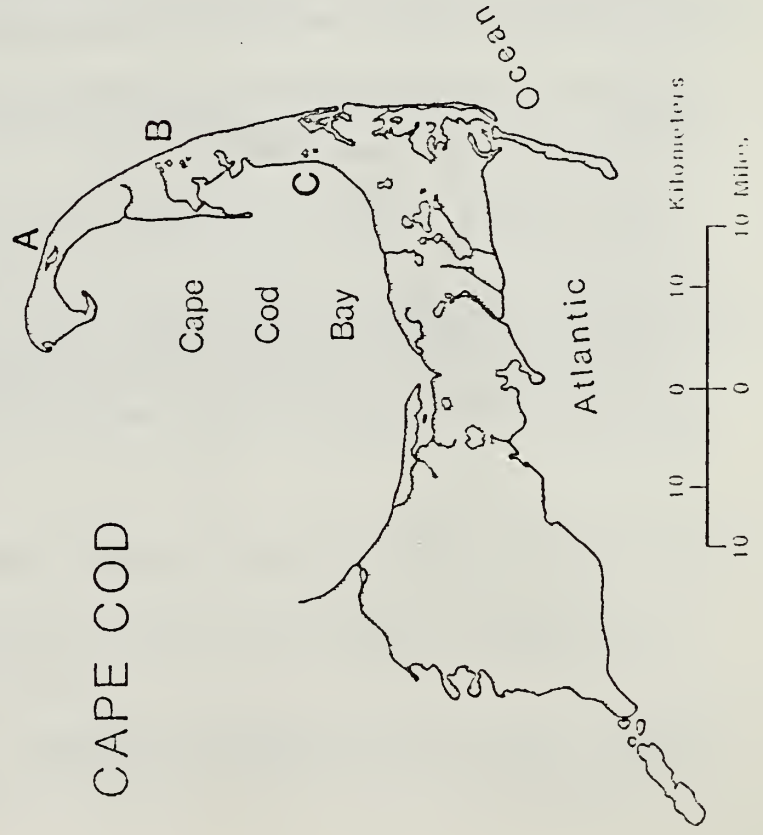
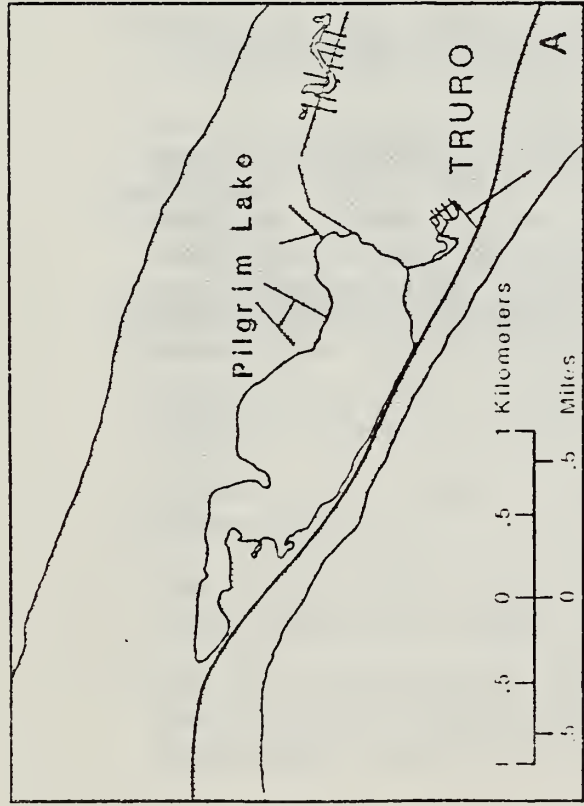


Fig. 1. Maps of Cape Cod, and Eastham, Wellfleet, Truro, Outer Cape Ponds.

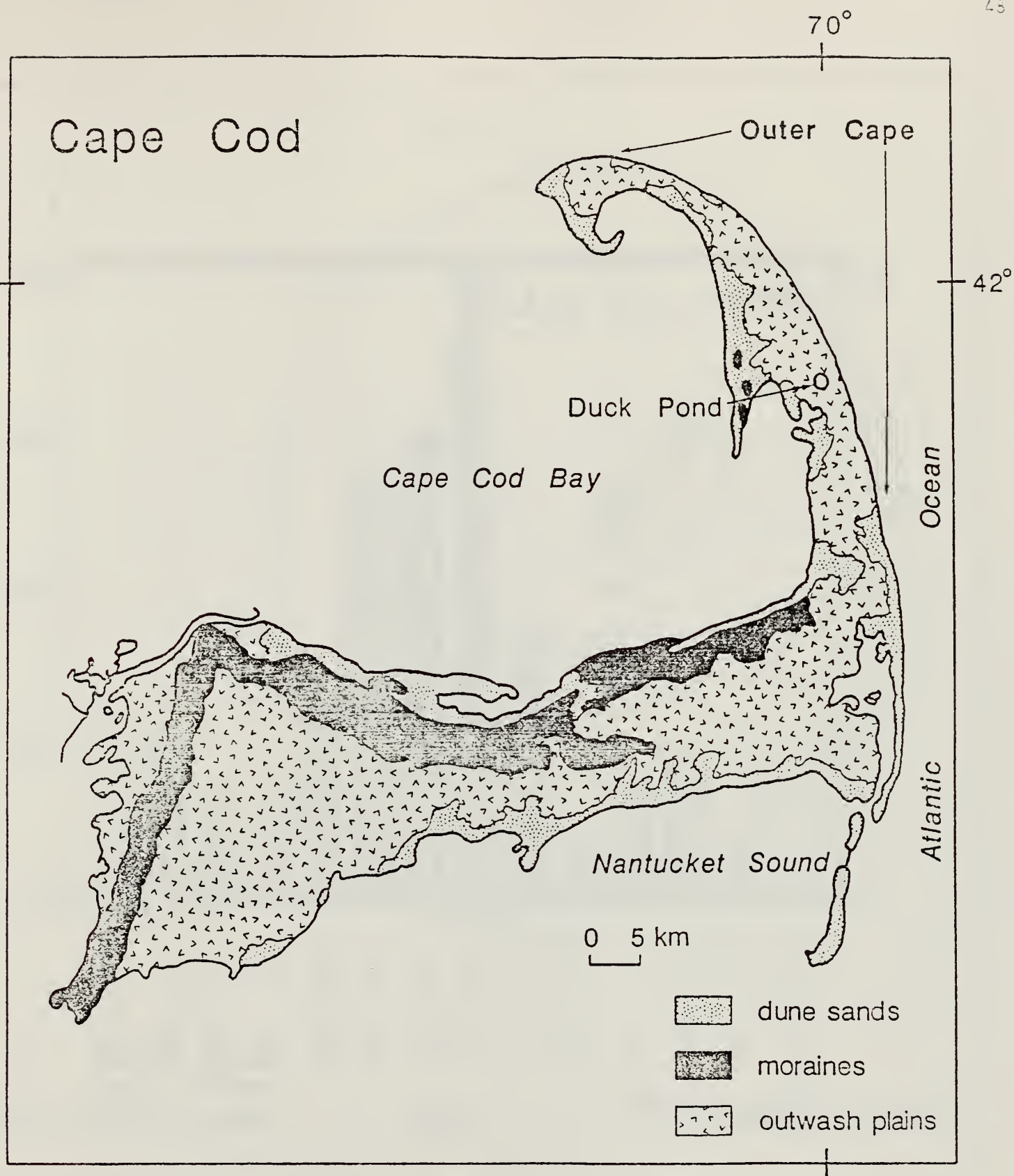


Fig. 2. Map of geologic and edaphic characteristics: Cape Cod.



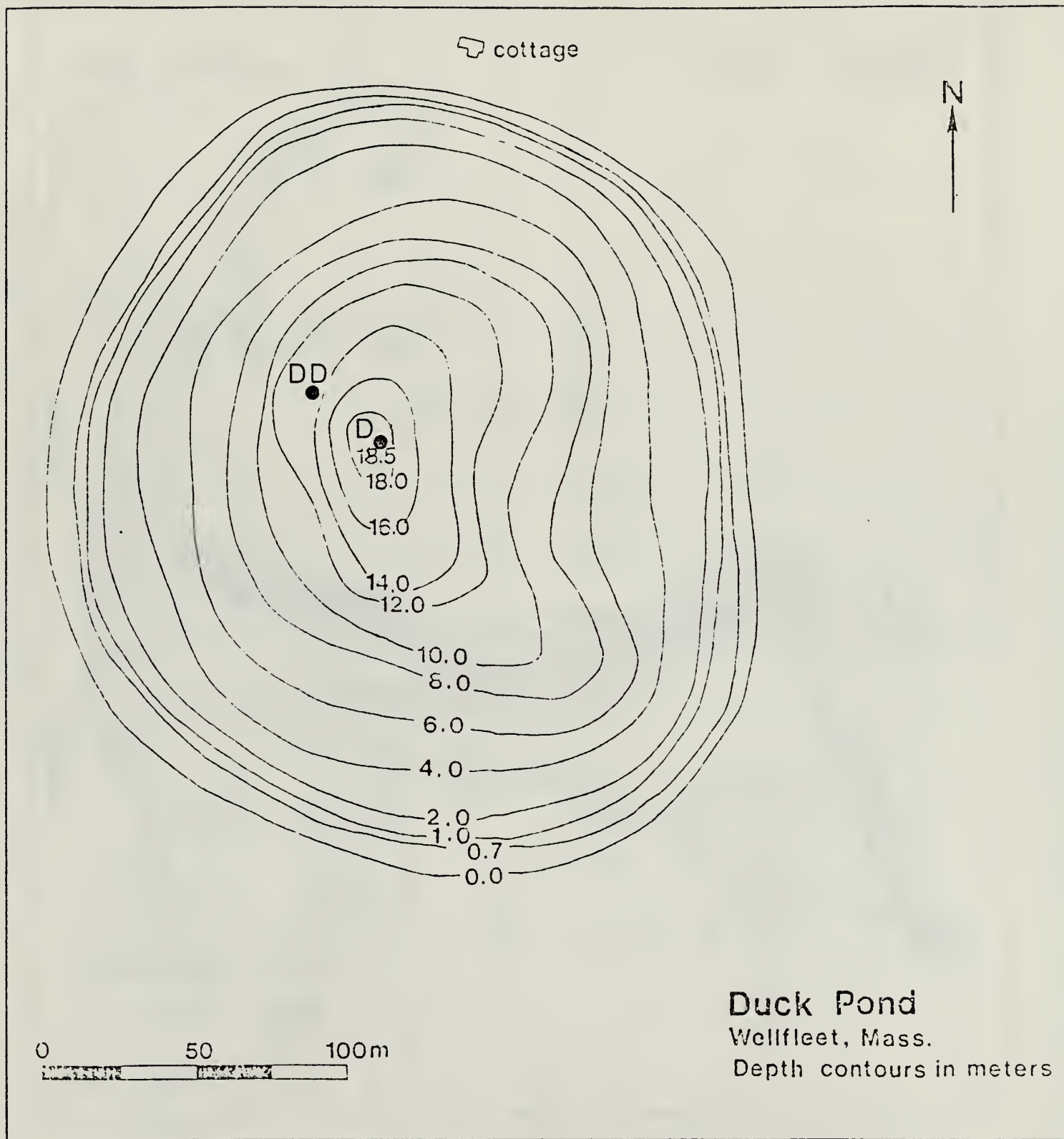


Fig. 3. Bathymetric map of Duck Pond showing position of coring sites D and DD. Map was provided by M. A. Soukup and J. Portnoy.

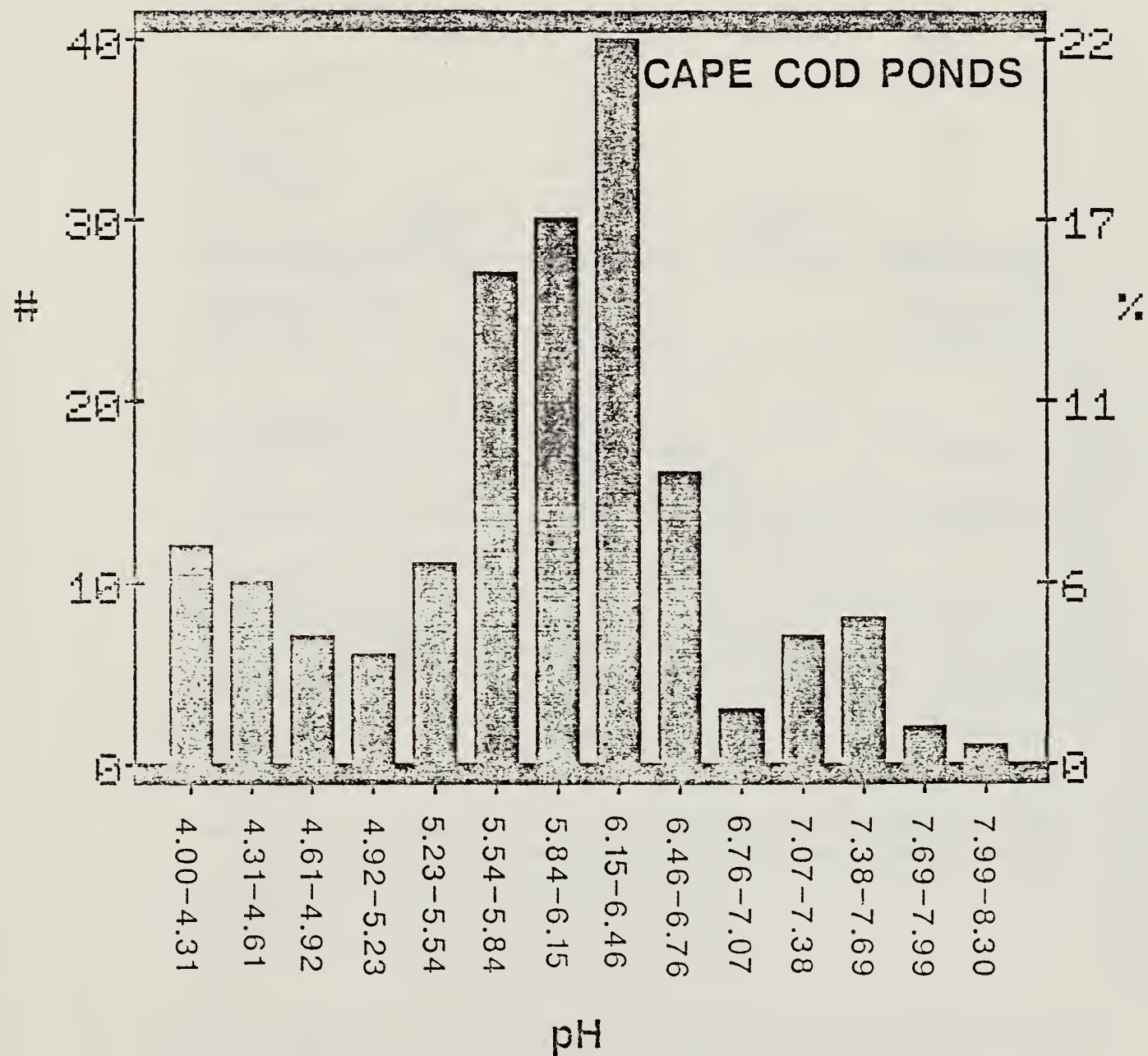


Fig. 4. pH frequency distribution: 180 Cape Cod Ponds. Data from the 1975 208 Water Quality Survey, provided by B. Peterson.

## Outer Cape Ponds

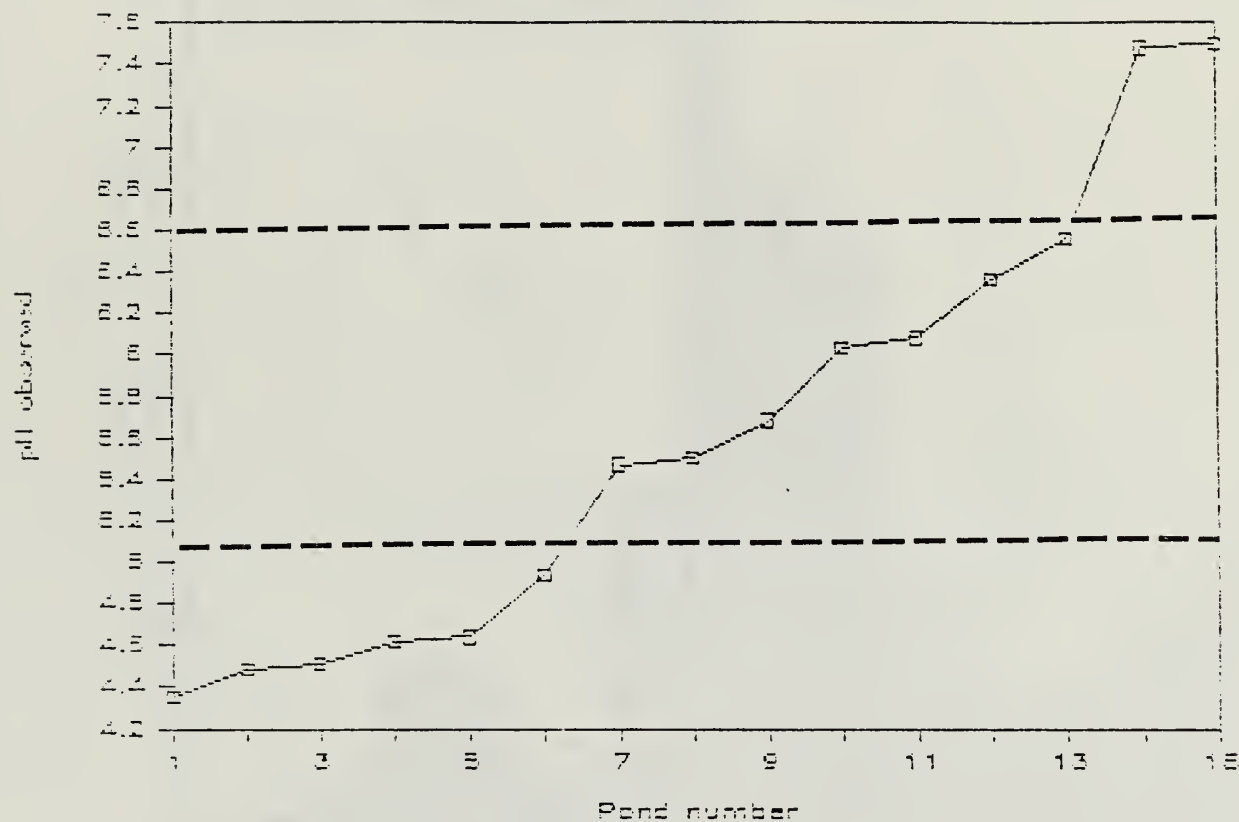


Fig. 5. pH distribution: Outer Cape Ponds. Mean pH was calculated from pH measurements taken at intervals from 9/75 to 5/84.

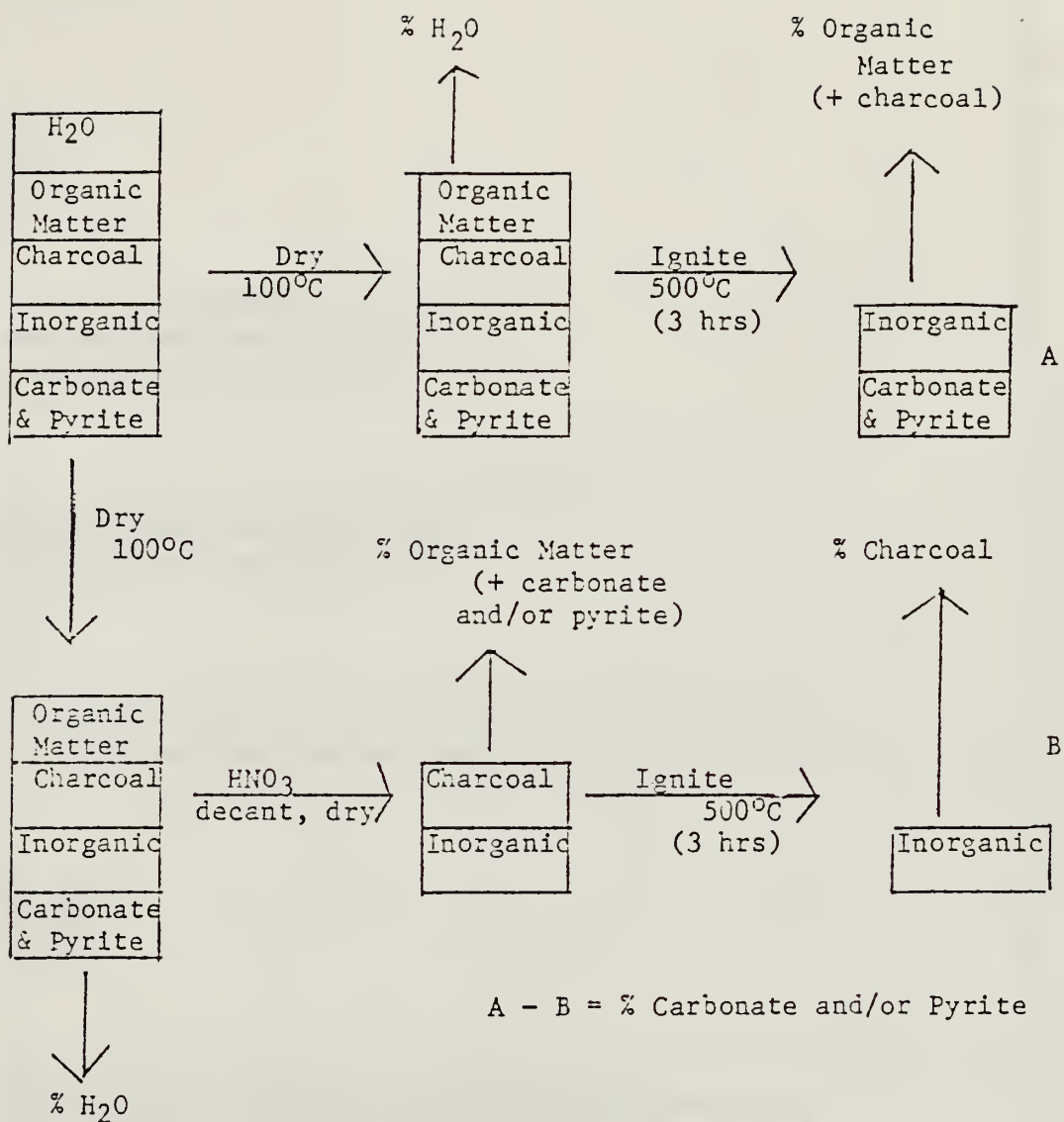


Fig. 6. Flow chart for sampling and chemical analysis of lake and bog sediments.



# Duck Pond Modern Diatom Percentages:

Three samples, 7 taxa

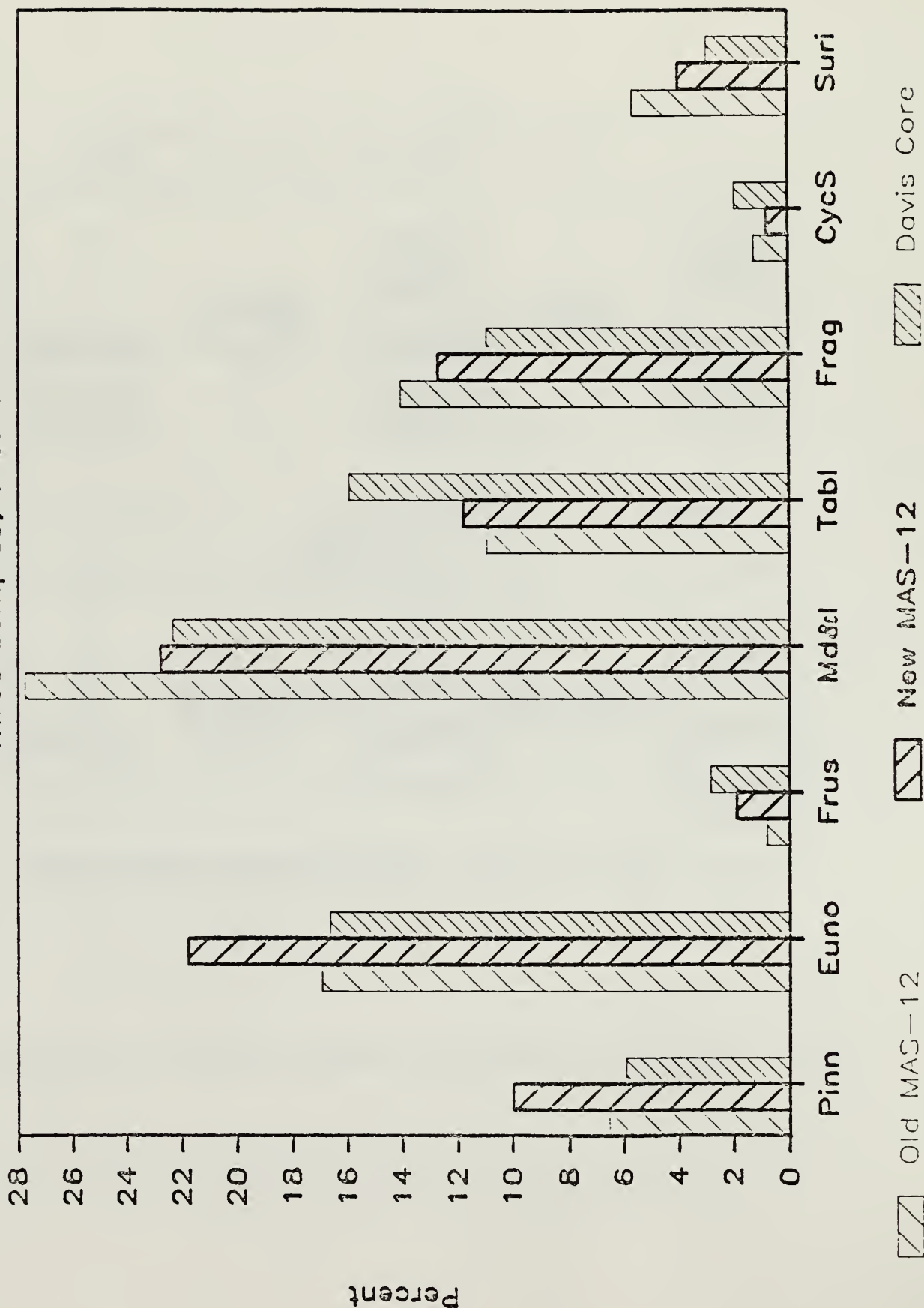


Fig. 7. Duck Pond modern diatom percentages: A comparison of 3 counts, 7

Morphometric and Chemical Analysis  
Modern Sediment Samples  
Cape Cod National Seashore Ponds  
Eastham, Westfleet, and Truro, Massachusetts

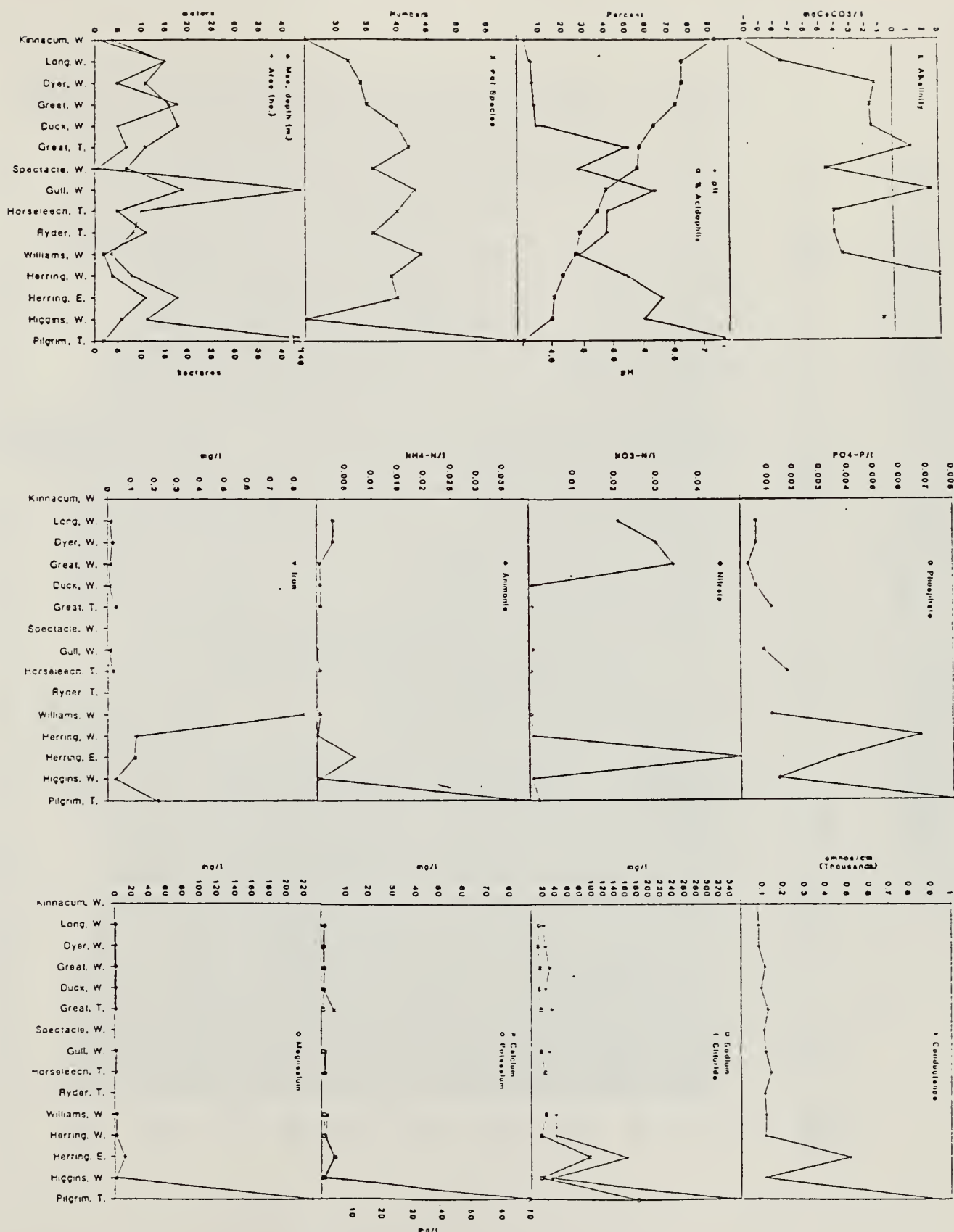


Fig. 8. Morphometry, chemistry of pondwater, and diatoms from modern sediment samples: Outer Cape Ponds. All of the ponds lie 2.5m or less above mean sea level and at about 42°N, 70°W (Fig. 2).

M

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# Outer Cape Ponds: Diatom pH Groups

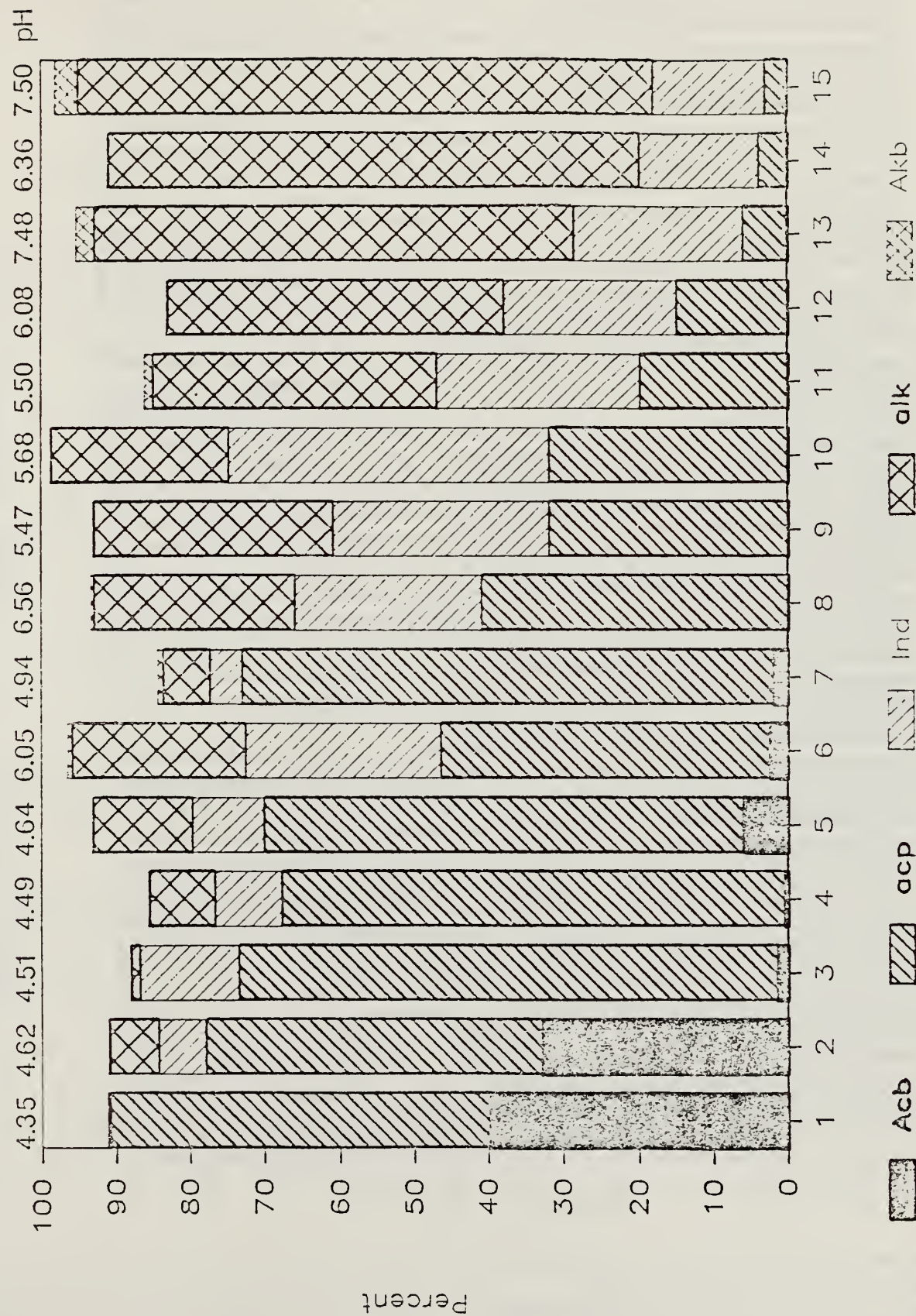


Fig. 10. Diatom pH Groups: Outer Cape Ponds. The pH value on this diagram is the mean pH calculated from all the measurements for each pond. Acb = Acidoblonts, acp = acidophils, Ind = indifferent (circum-neutral), alk = alkaliphils, Akb = Alkaliblonts.



# Outer Cape Ponds

Diatom Habitat Groups

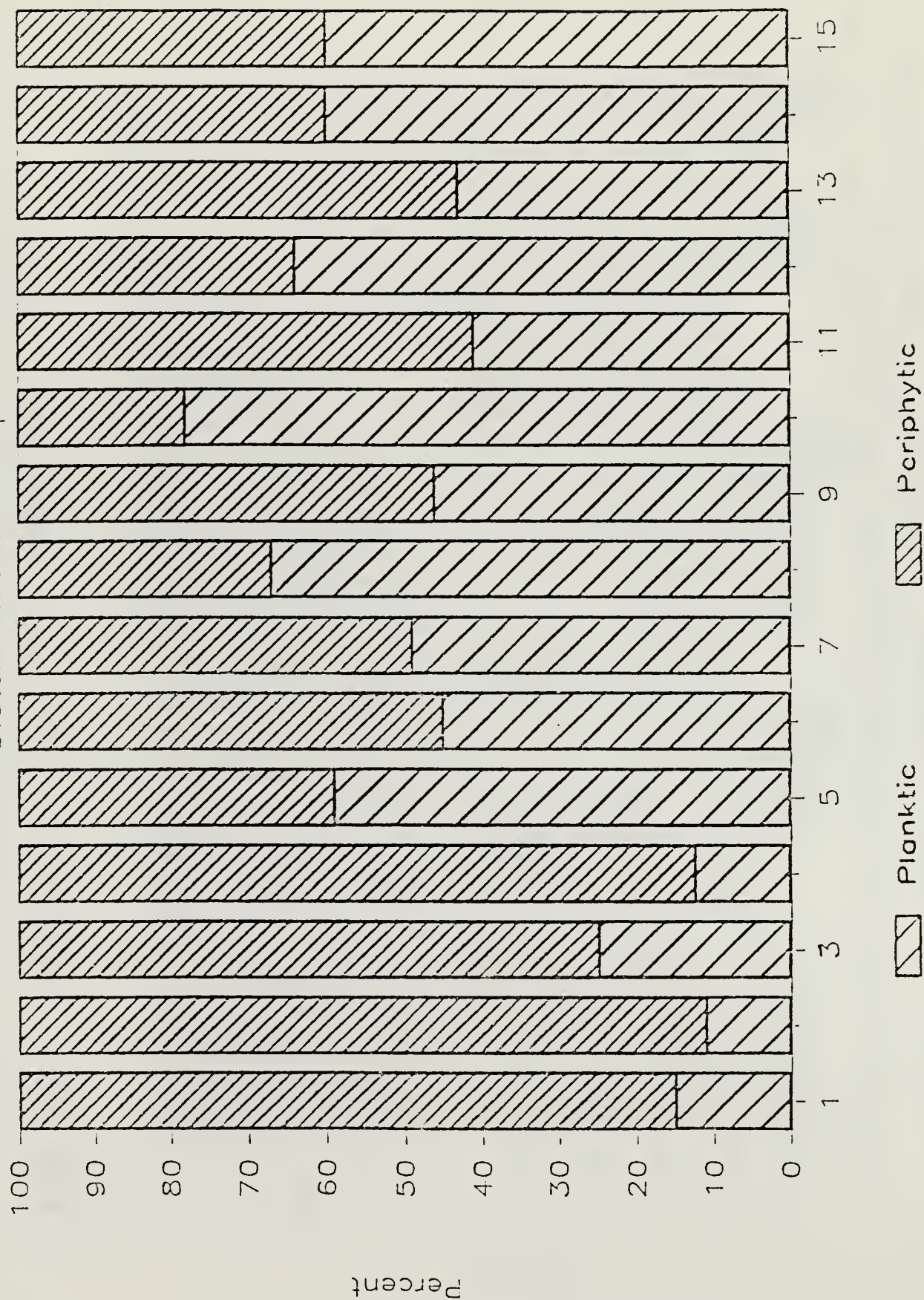


Fig. 11. Diatom Habitat Groups: Outer Cape Ponds.

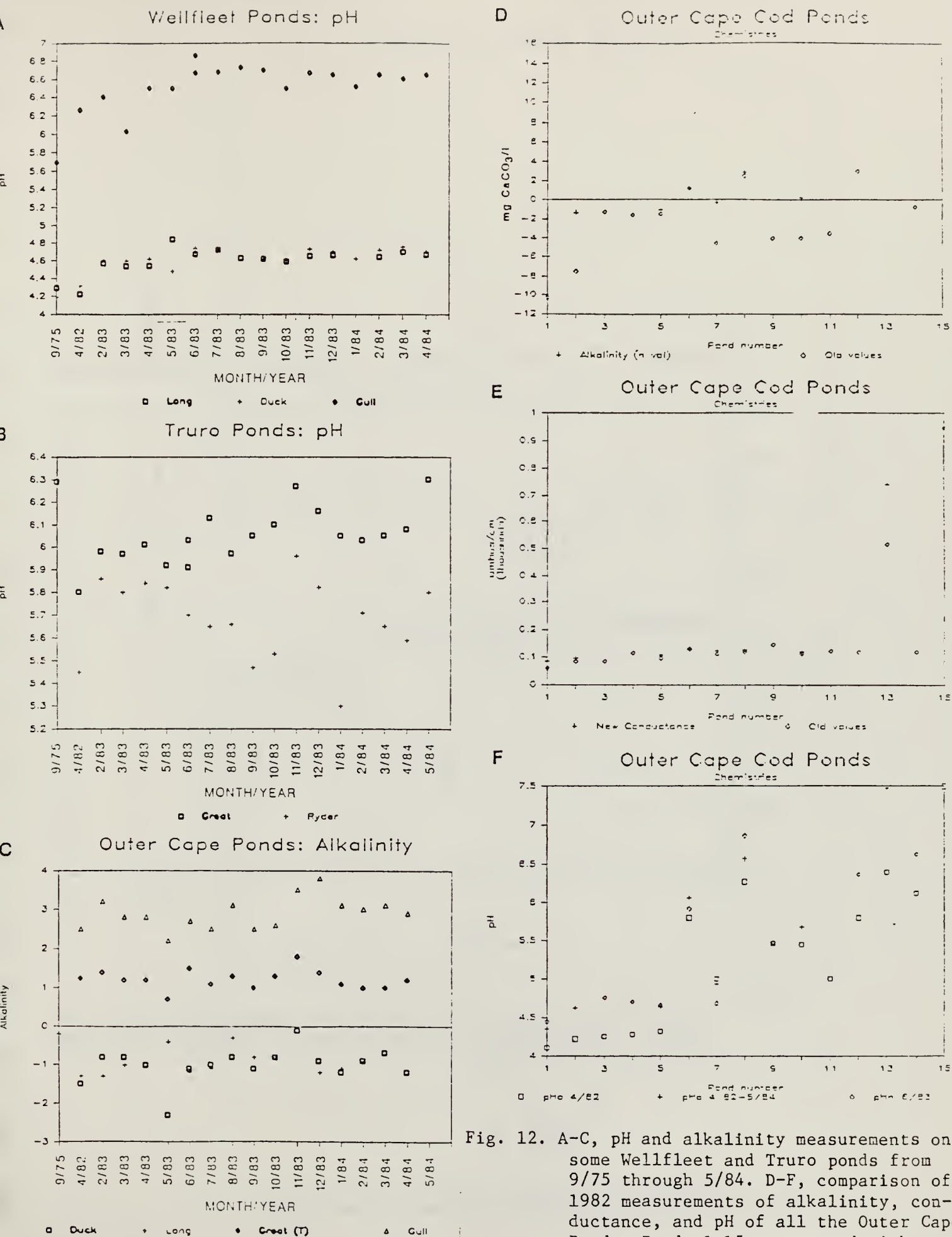


Fig. 12. A-C, pH and alkalinity measurements on some Wellfleet and Truro ponds from 9/75 through 5/84. D-F, comparison of 1982 measurements of alkalinity, conductance, and pH of all the Outer Cape Ponds. Ponds 1-15 correspond with pond order in Fig. 8.

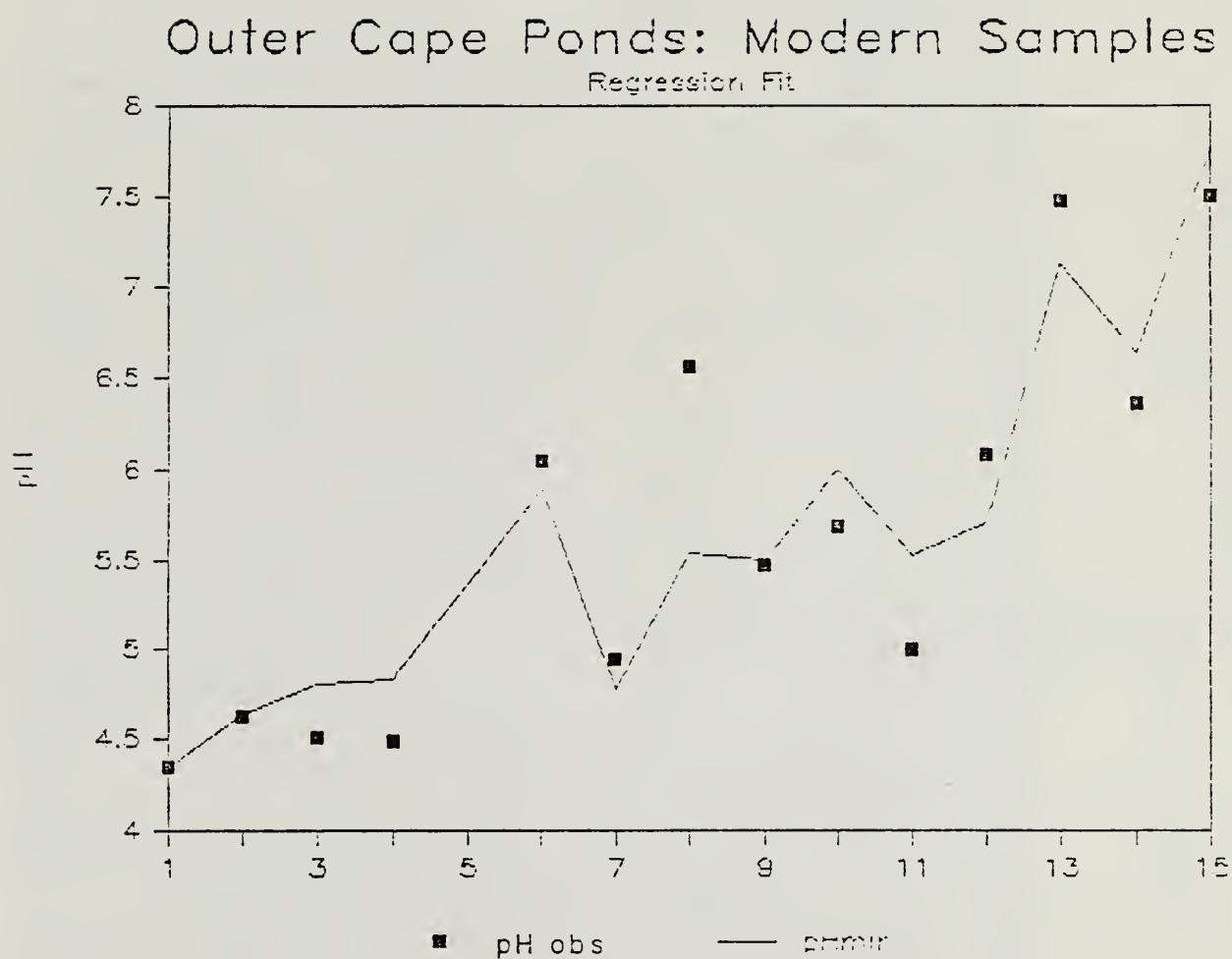
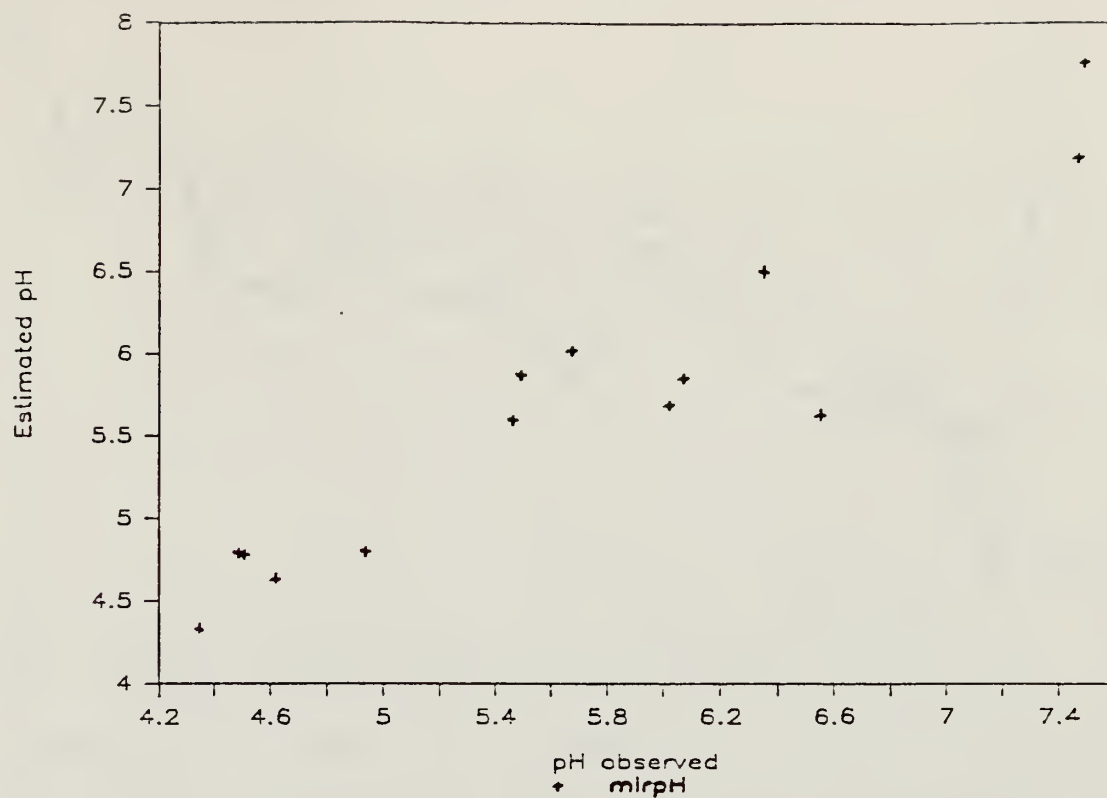


Fig. 13. Regression fit: pH observed and pH estimated for the Outer Cape Ponds. Ponds numbered in order of Fig. 8. Equation used (mlrpH) is presented in Table 4.

A

## OUTER CAPE PONDS



B

## OUTER CAPE PONDS

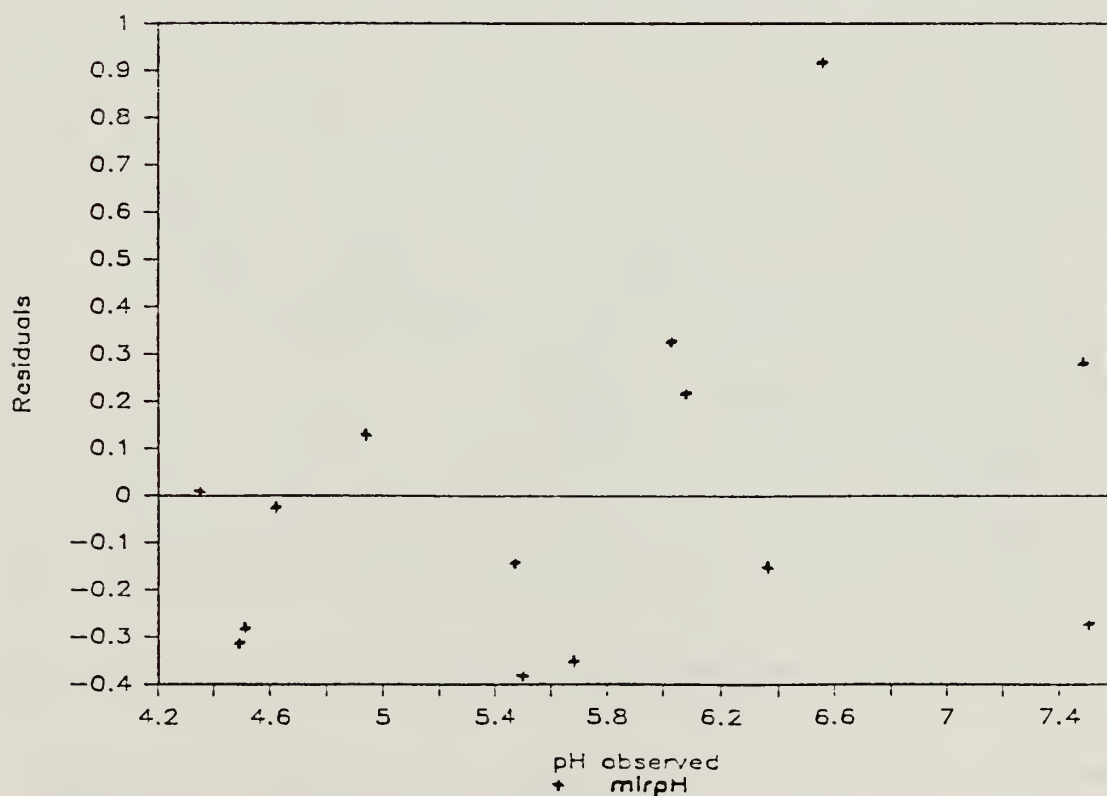
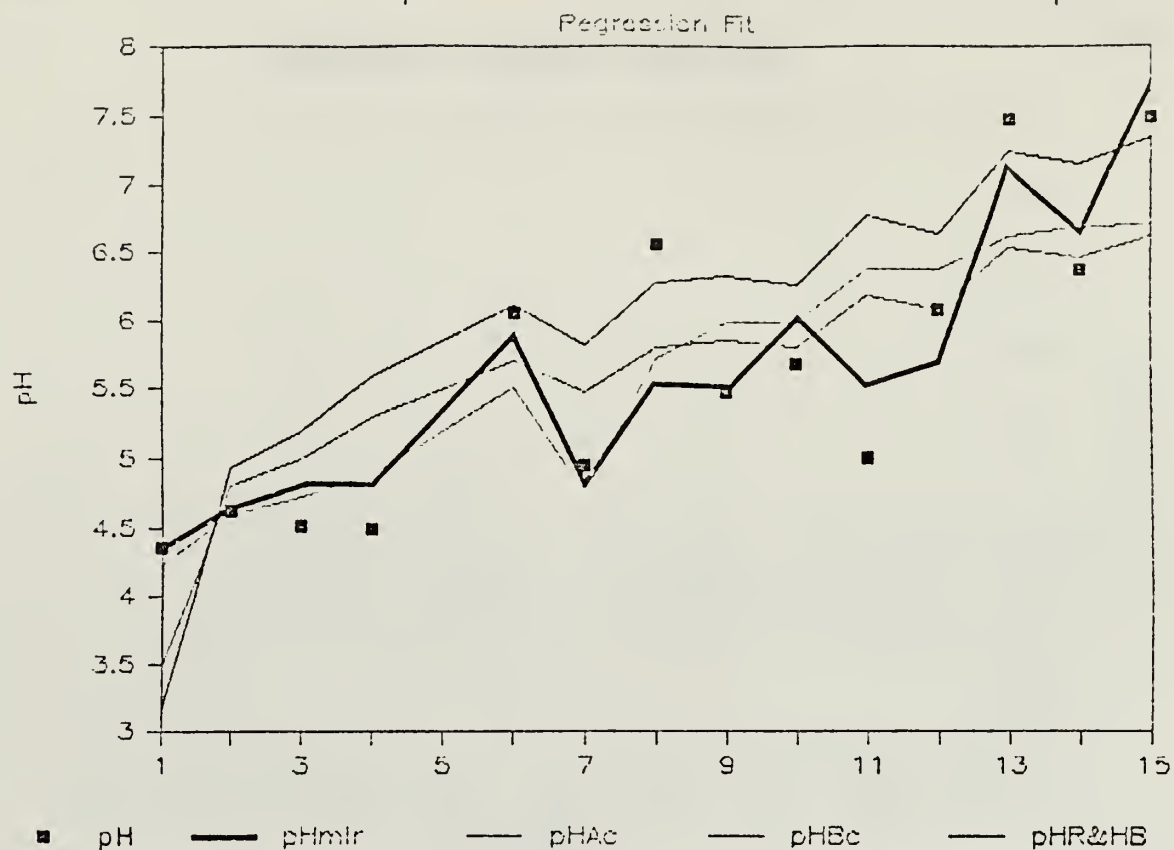


Fig. 14. A. Plot of pH estimated against pH observed.  
B. Estimation residuals plotted against pH observed.





B Outer Cape Ponds: Modern Samples

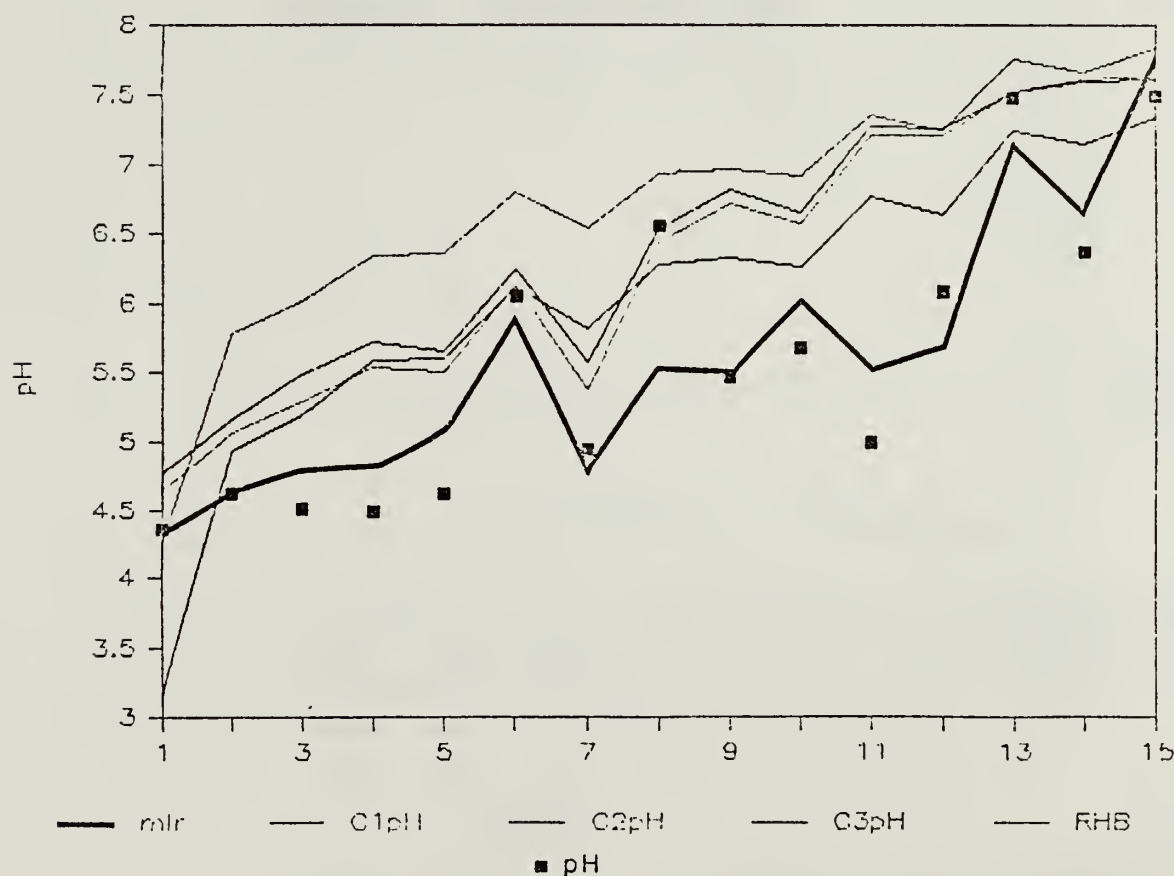


Fig. 15. A.&B. Regression fit for several other equations. RHB (Renberg and Hellberg, 1982); C1pH, C2pH, C3pH (Charles, 1985a); pHAc and pHBc (Winkler, unpubl data). pHmlr(mlr) is used in this study (Table 4) and pH is the observed value for the Outer Cape Ponds.

DEPTH IN CENTIMETERS

450	400	350	300	250	200	150	100	50	0	D	D
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# DUCK POND, S. Wellfleet, Massachusetts

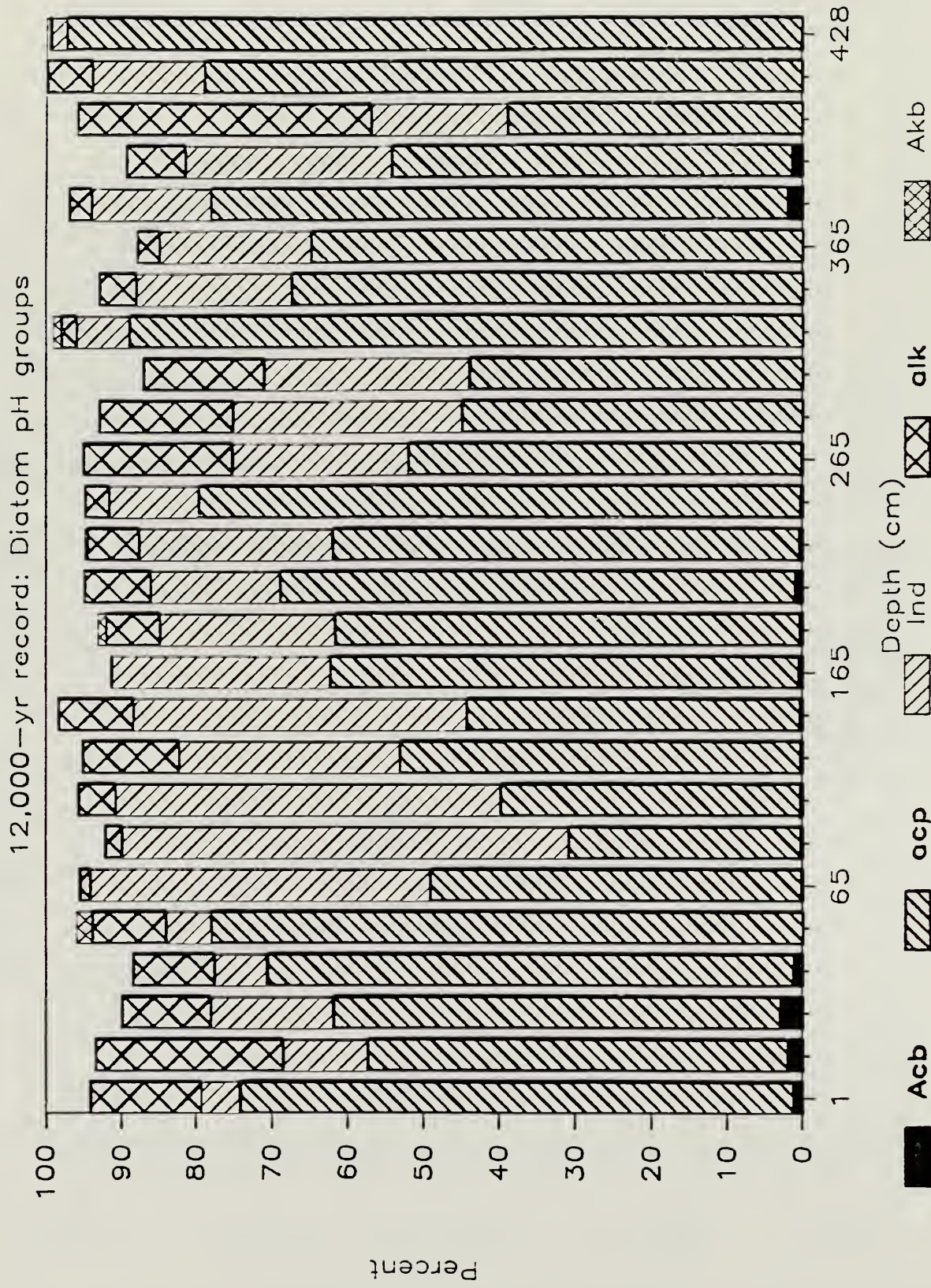


Fig. 17. Duck Pond Core D: Diatom pH groups.  
 Acb = Acidobionts, acp = acidophils, Ind = indifferent (circum-neutral), alk = alkaliphils, Akb = Alkalibionts.



# DUCK POND, S. Wellfleet, Massachusetts

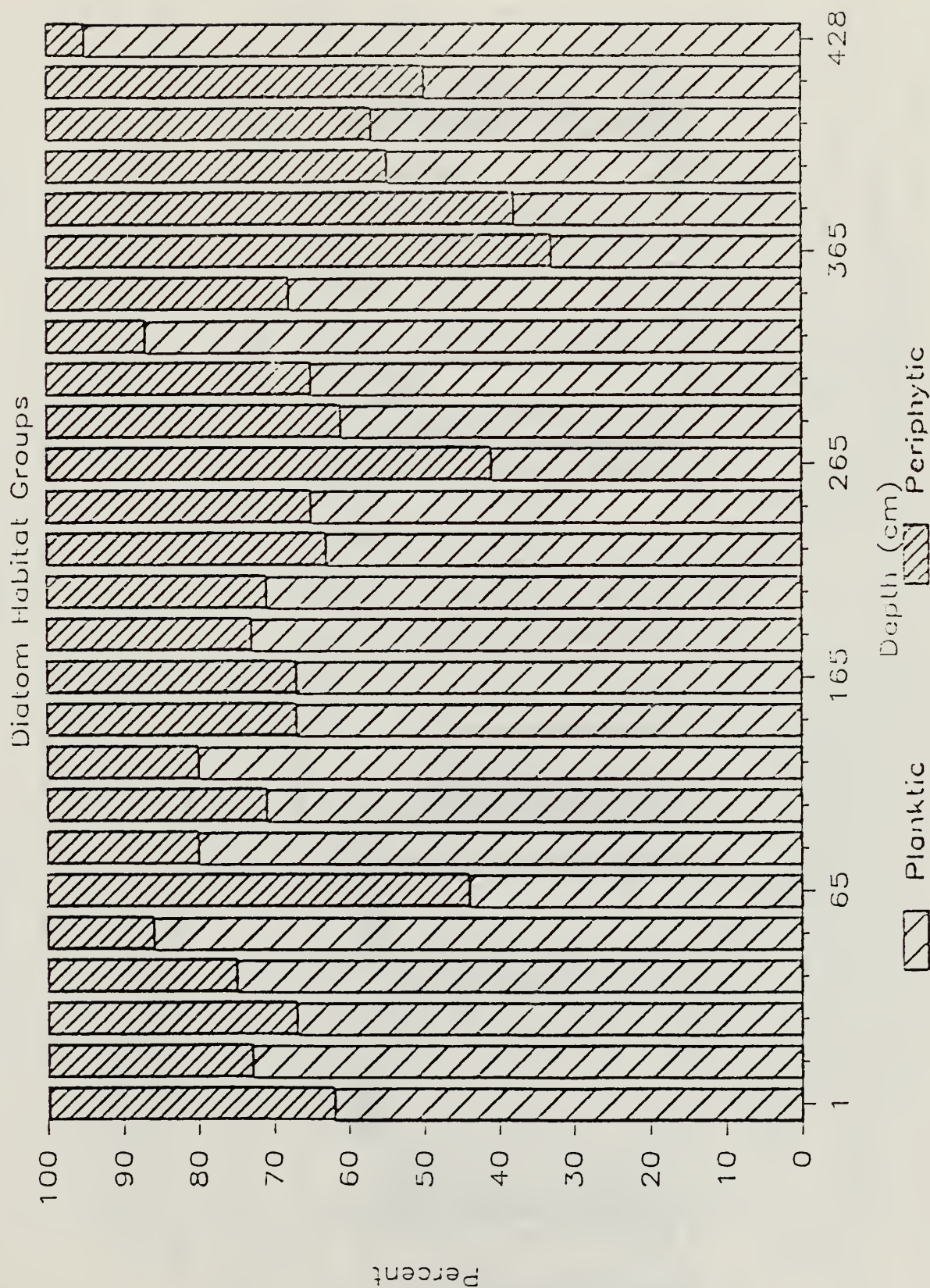


Fig. 18. Duck Pond Core D: Diatom habitat groups.



DUCK POND

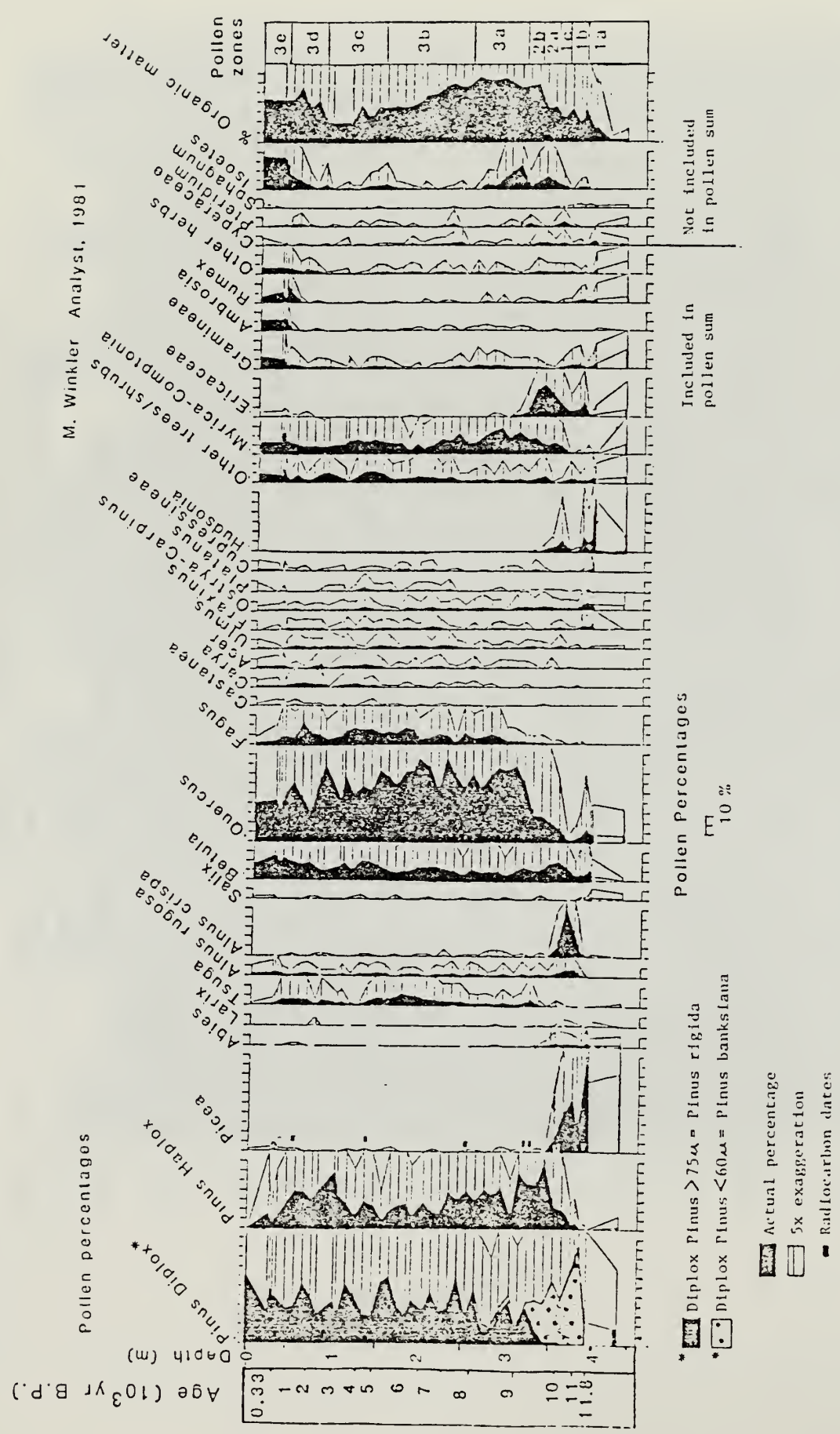
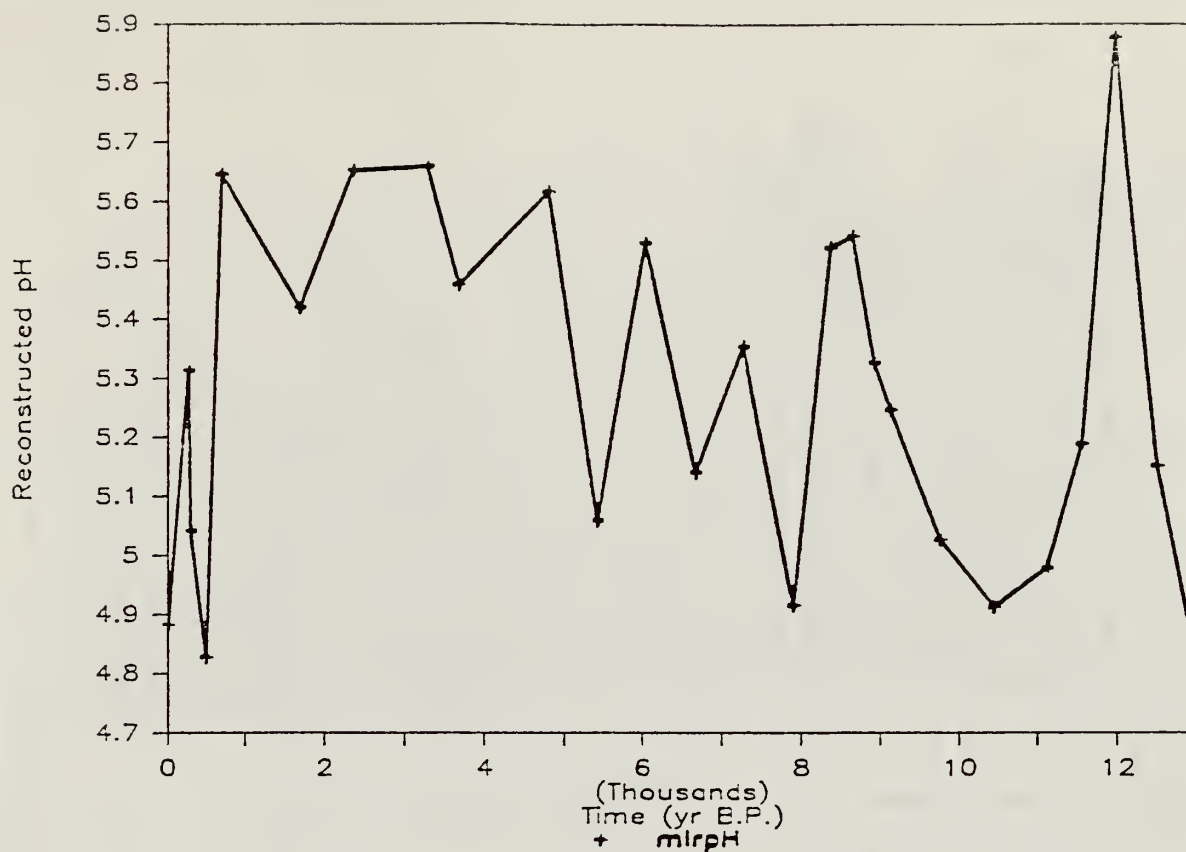


Fig. 19. Duck Pond Core D: Pollen percentage diagram (Winkler, 1985a).

A

## Duck Pond



B

## Duck Pond

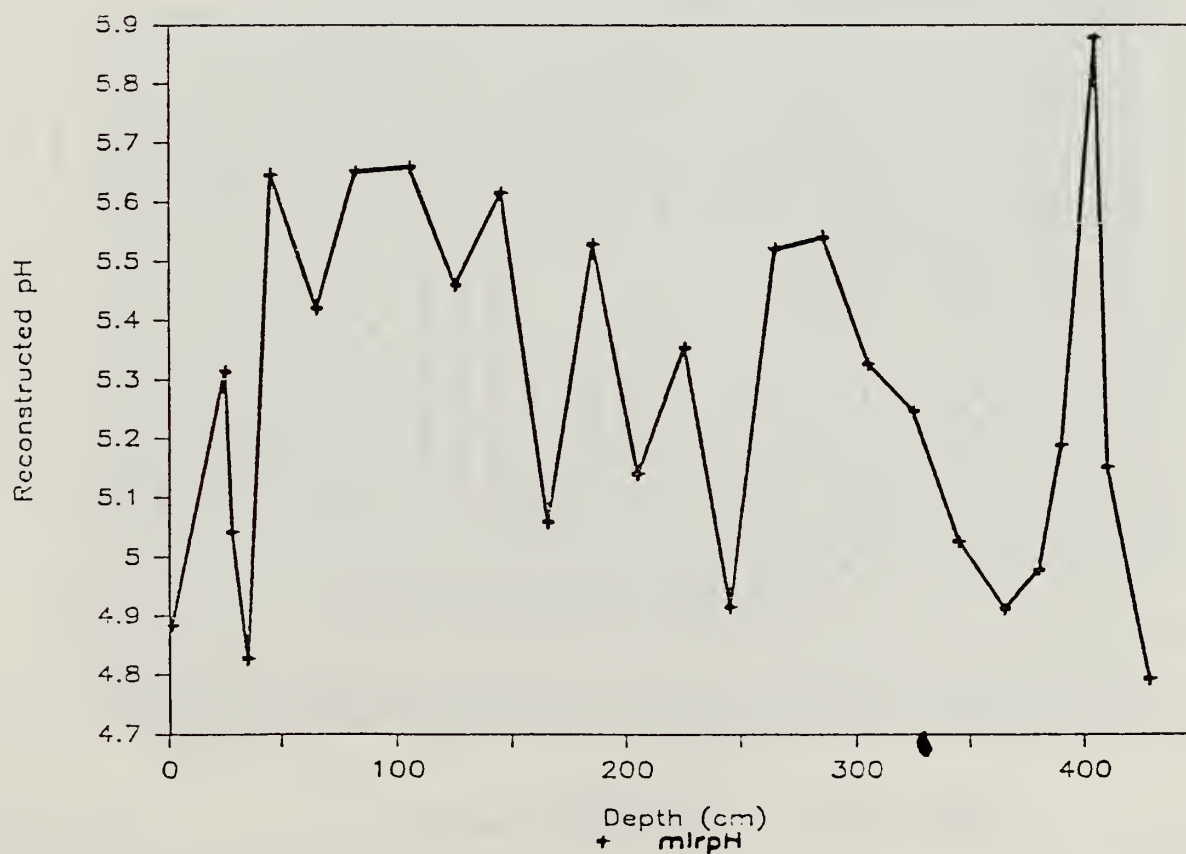


Fig. 20. Reconstructed pH of Duck Pond using Core D diatoms and diatom-pH transfer function (Table 4.). A. Time scale. B. Depth scale.

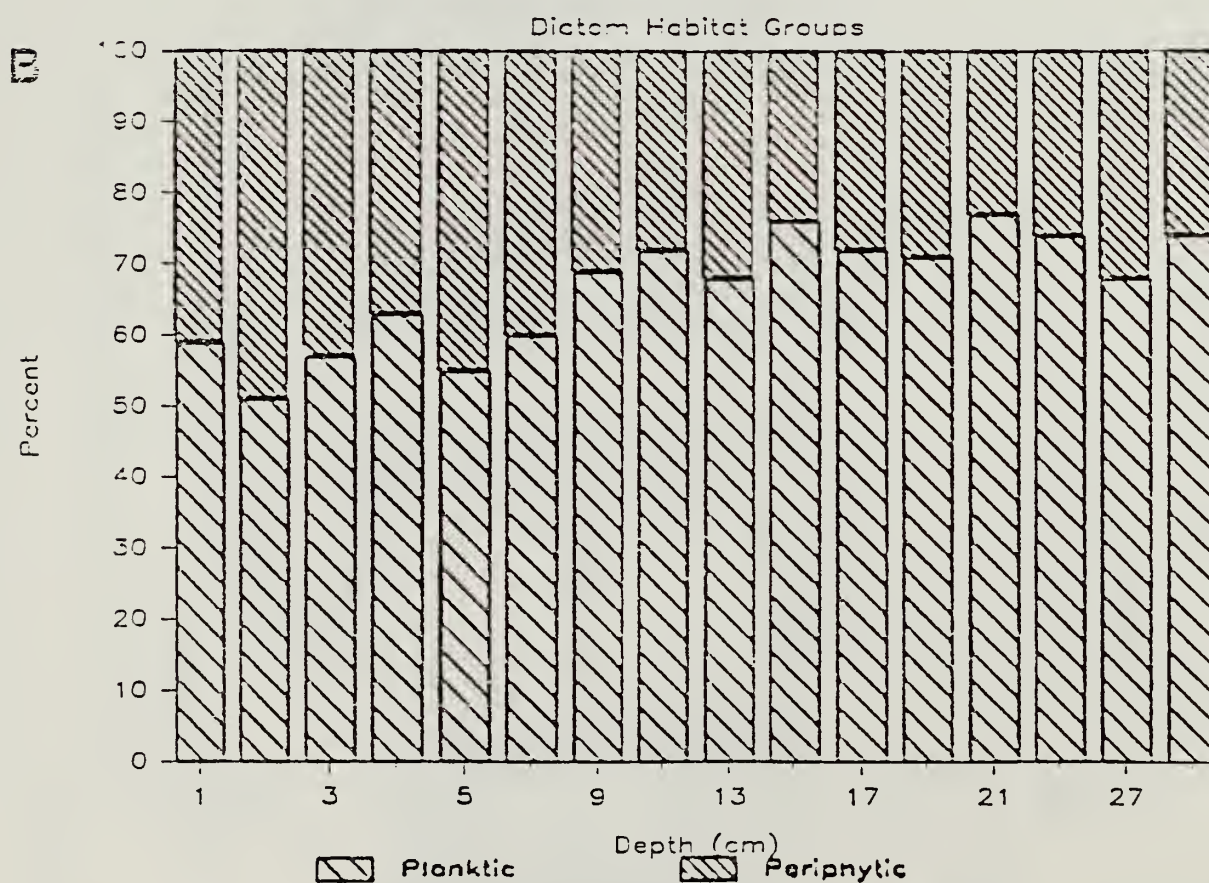
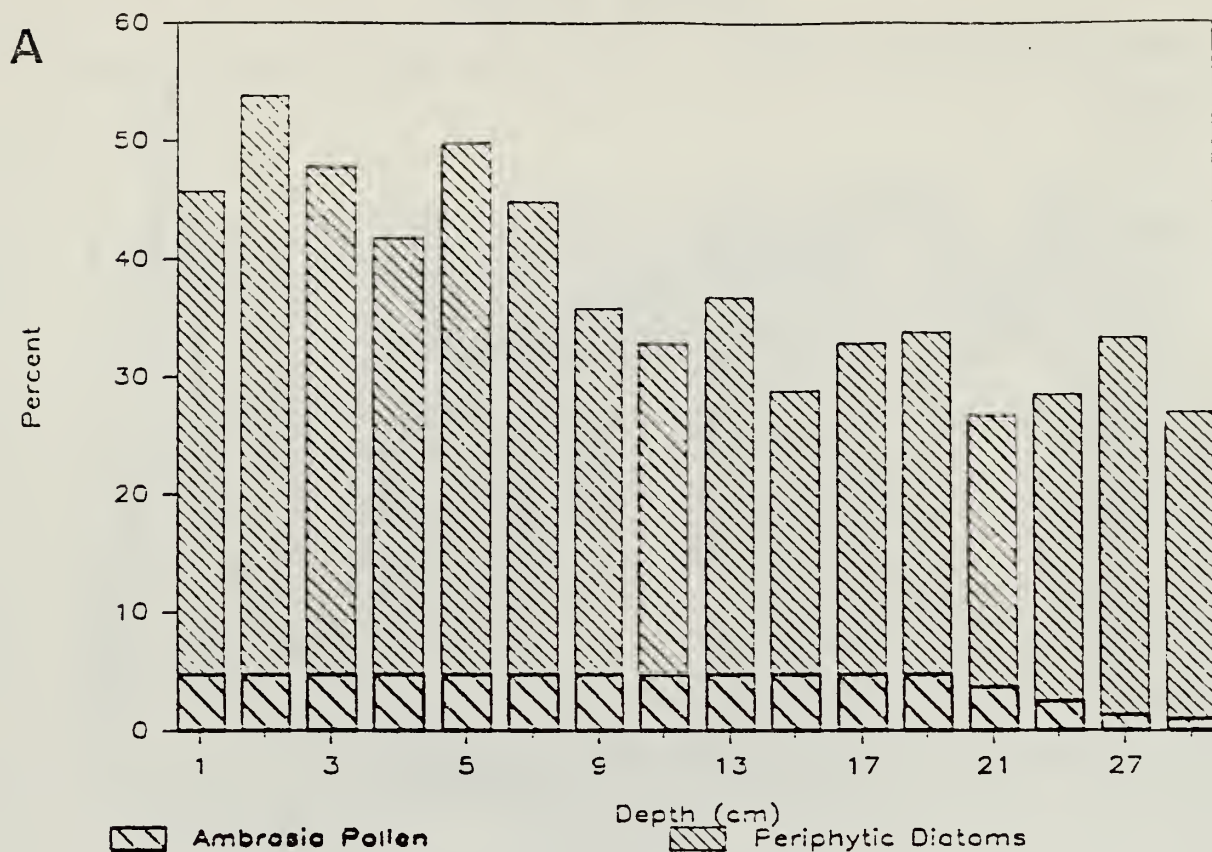


Fig. 21. Duck Pond post-European settlement core DD. A. Percentage of Ambrosia pollen in sediments suggests European settlement time-line at about 24 cm in core DD. B. Diatom habitat groups, core DD.



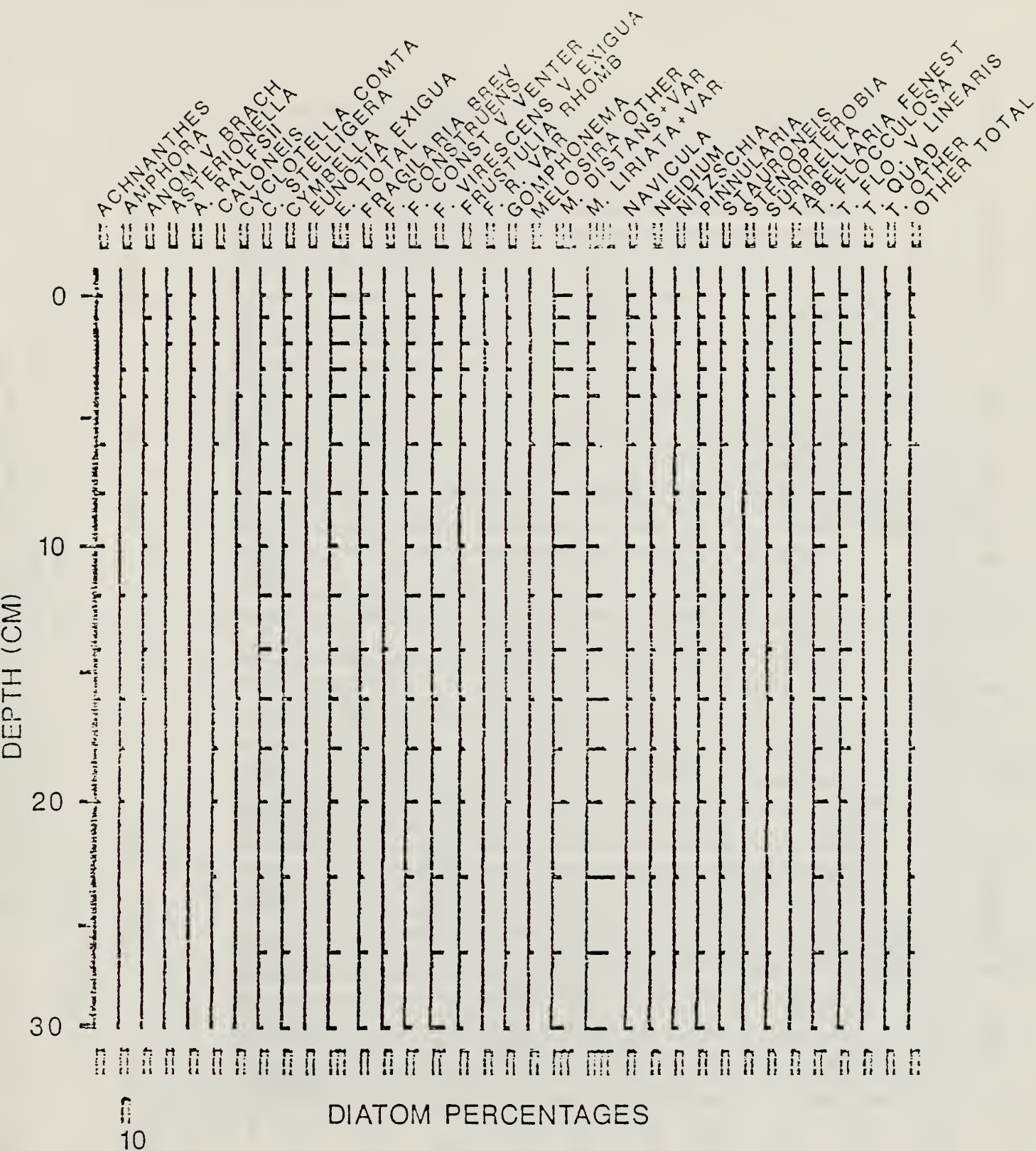


Fig. 22. Duck Pond post-European settlement core DD. Diatom percentage diagram.



# Duck Pond: Post-European Settlement

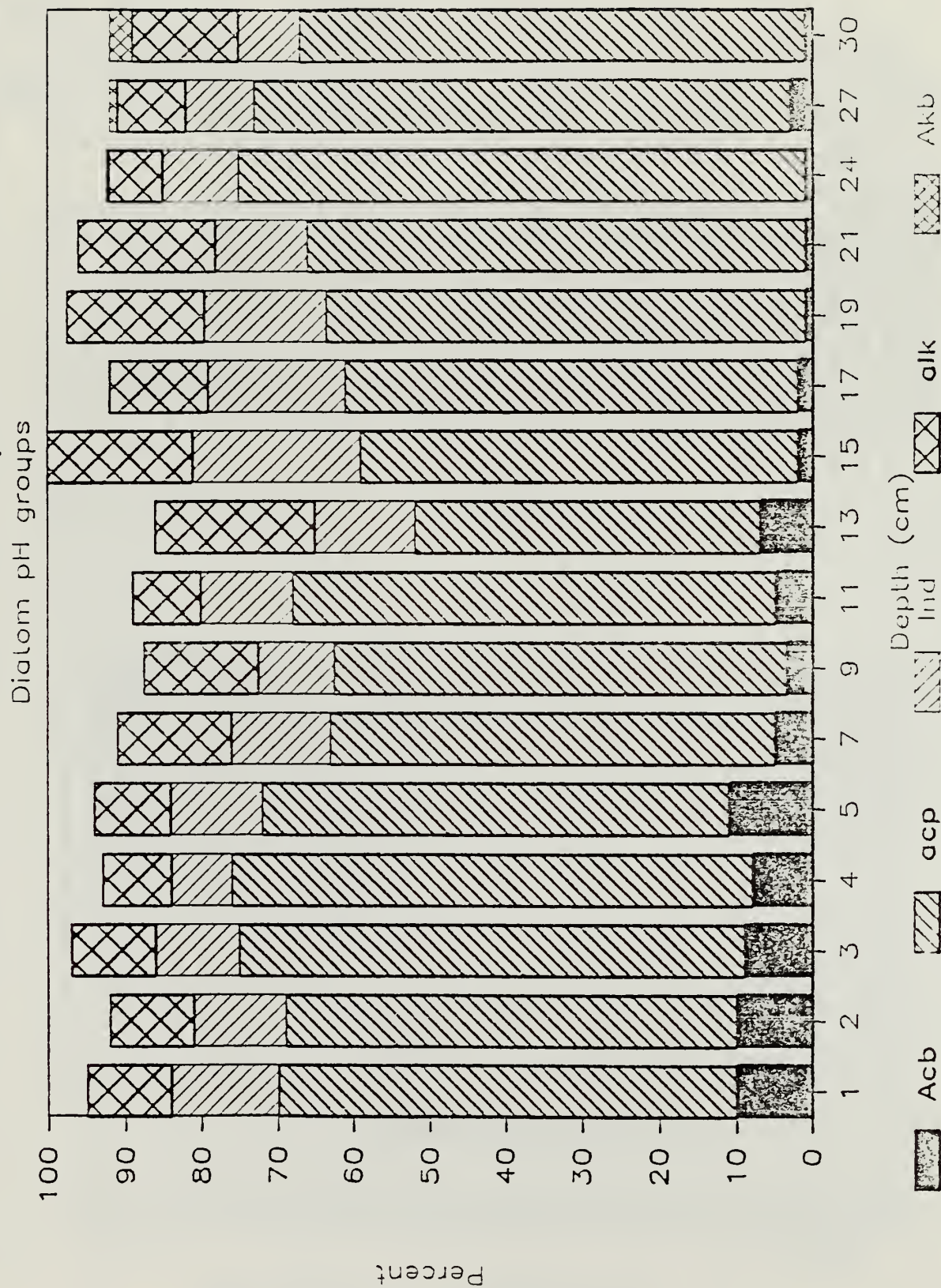
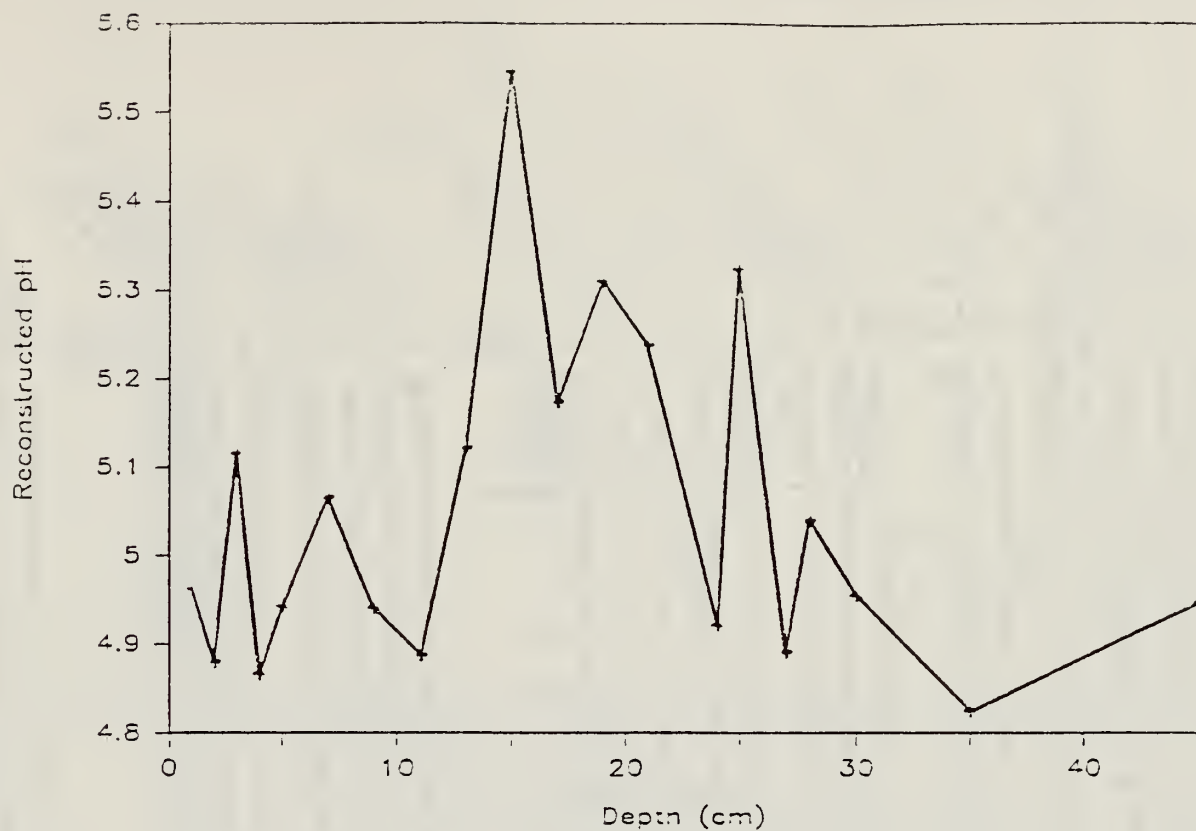


Fig. 23. Duck Pond post-European settlement core DD. Diatom pH groups.  
 Acb = Acidobionts, acp = acidophils, Ind = indifferent (circum-neutral), alk = alkaliphils, Akb = Alkalibionts.

# A Duck Pond, S. Wellfleet, Massachusetts



# B Duck Pond, S. Wellfleet, Massachusetts

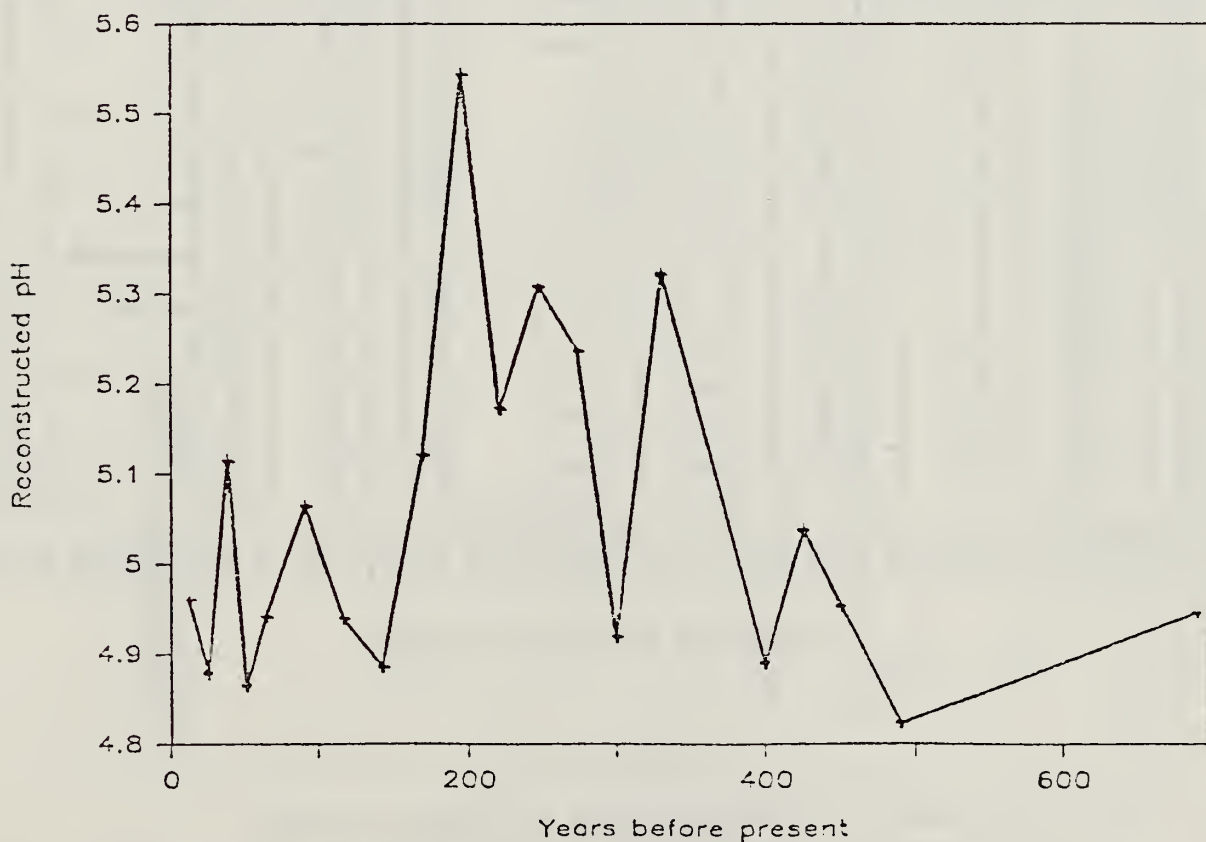


Fig. 24. Reconstructed pH of Duck Pond using Core DD diatoms and diatom-pH transfer function (Table 4.). A. Depth scale. B. Time scale.

Duck Pond Both Cores  
Diatom Percentages 1985

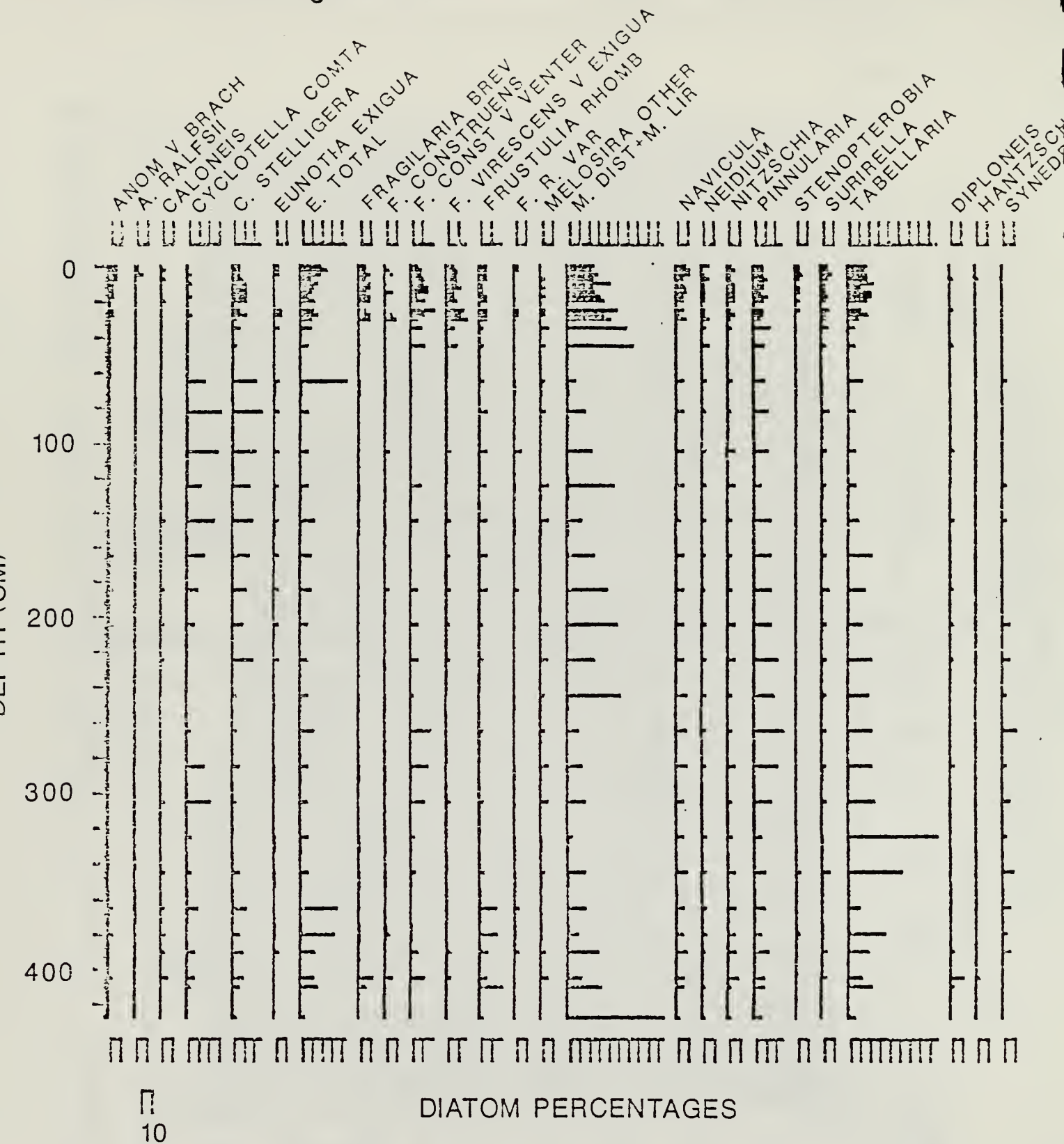
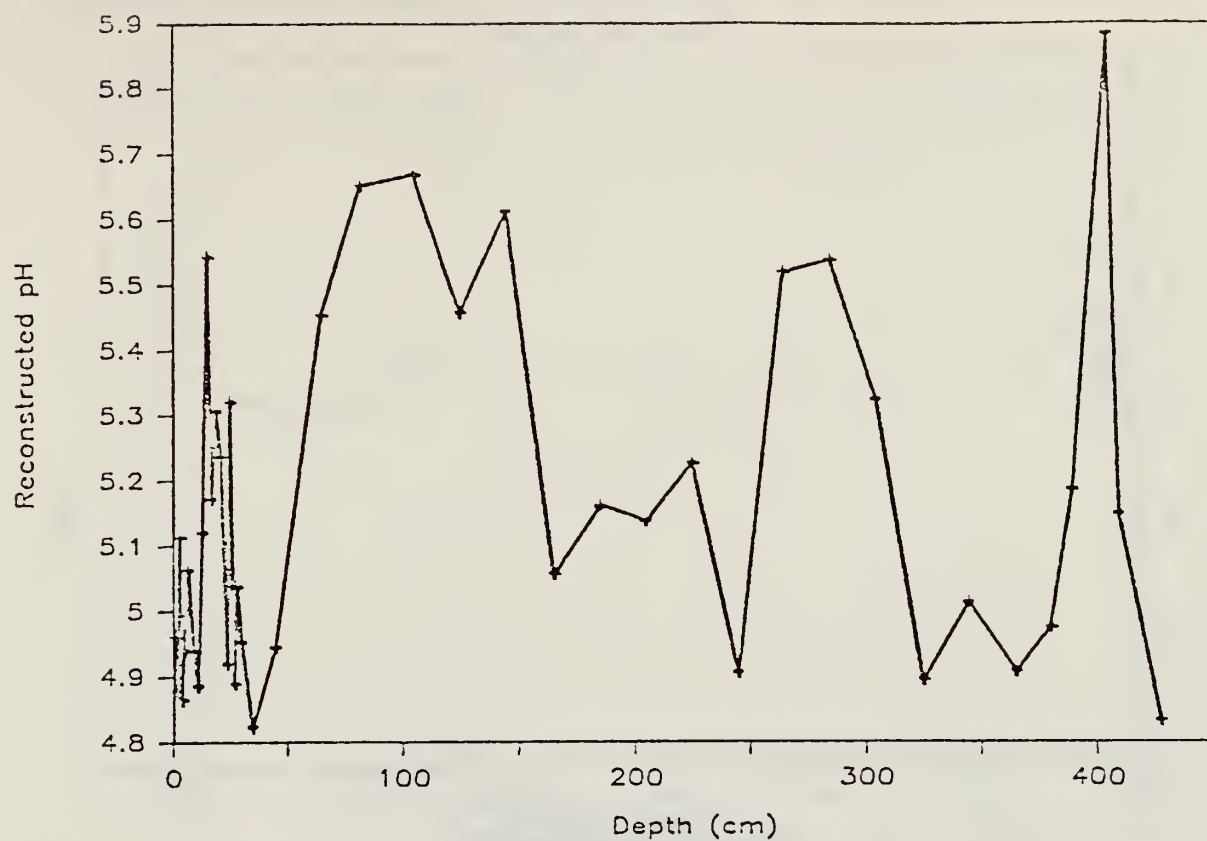
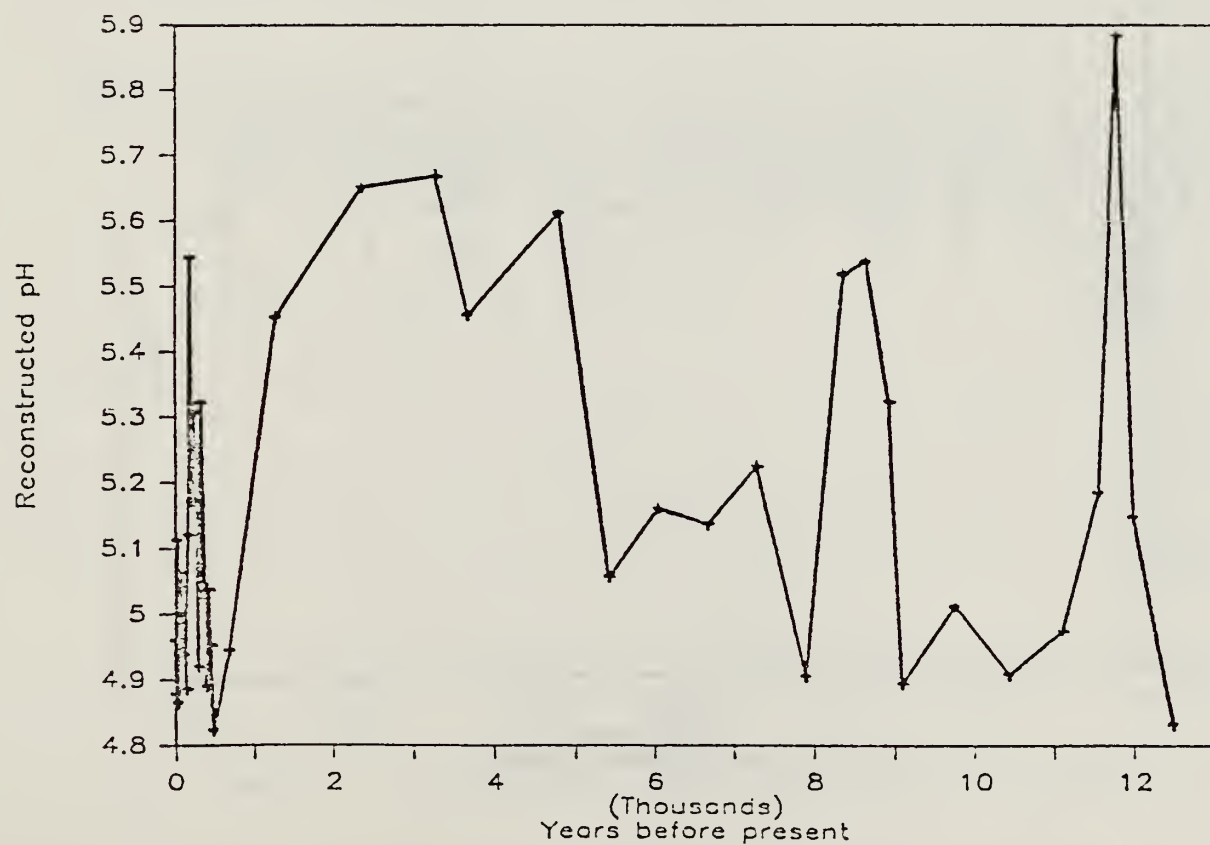


Fig. 25. A. Duck Pond, both cores: diatom percentage diagram.  
Reconstructed pH of Duck Pond using both cores and diatom-pH  
transfer function (Table 4.). B. Depth scale. C. Time scale.

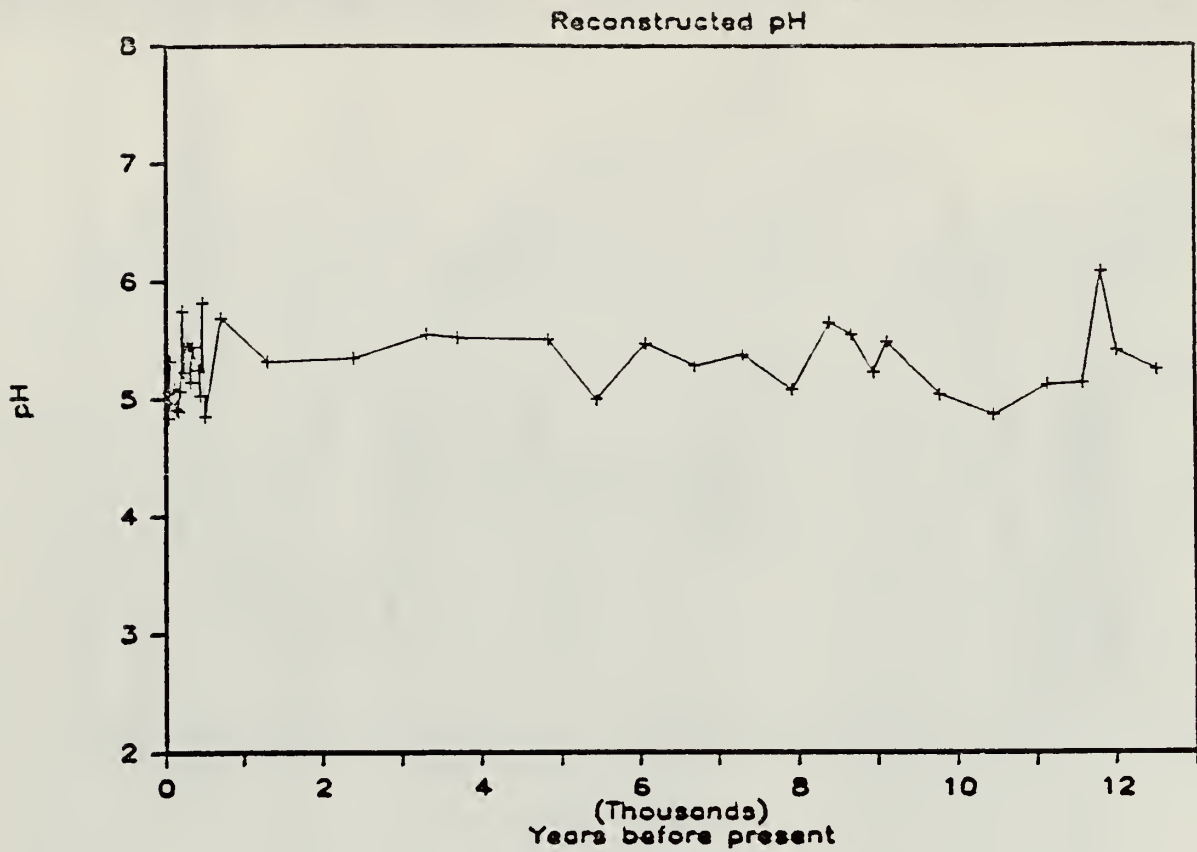


C Duck Pond, S. Wellfleet, Massachusetts





# A Duck Pond, S. Wellfleet, Massachusetts



# B Duck Pond, S. Wellfleet, Massachusetts

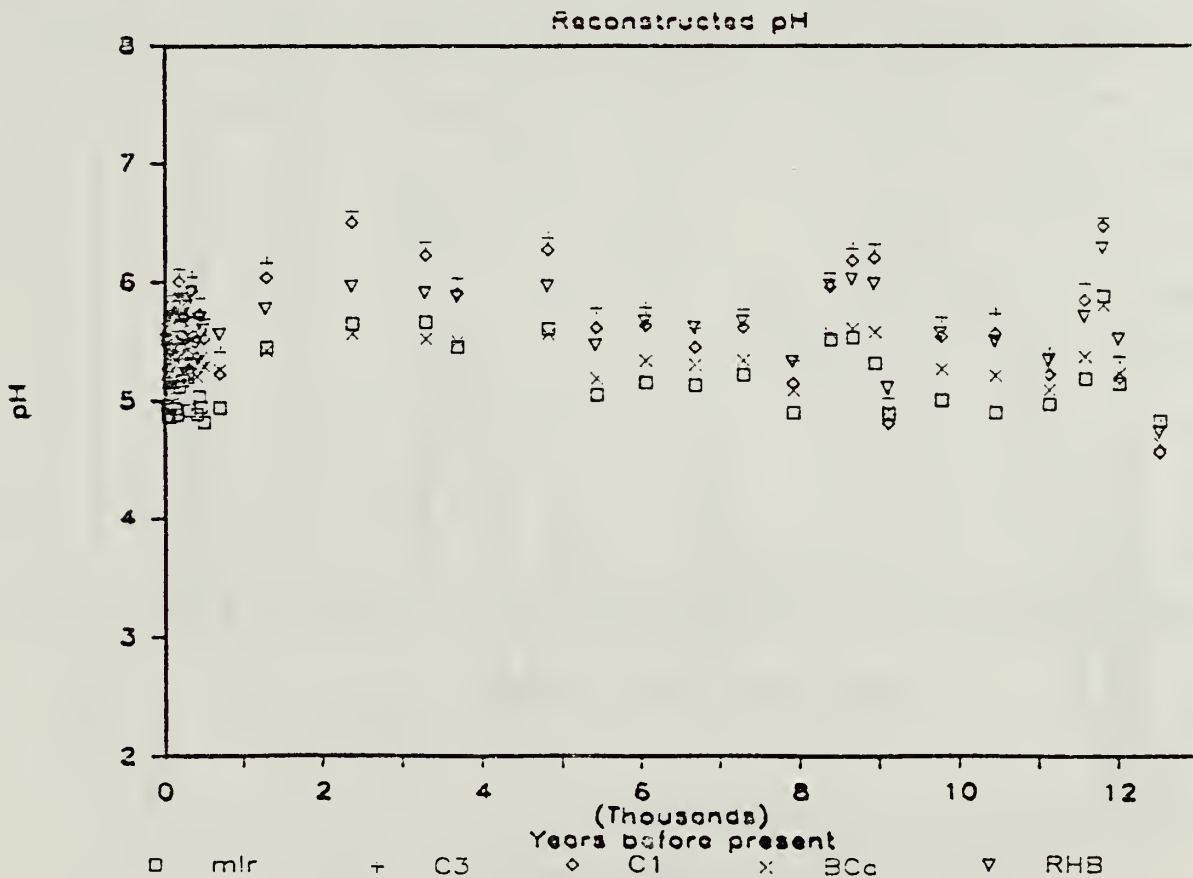


Fig. 26. A. Duck Pond, both cores: reconstructed pH, expanded pH scale.  
B. Duck Pond, both cores: reconstructed pH from other equations (see Fig. 15).

# PRECIPITATION CHEMISTRY: OUTER CAPE COD

12/15/81 to 7/02/85

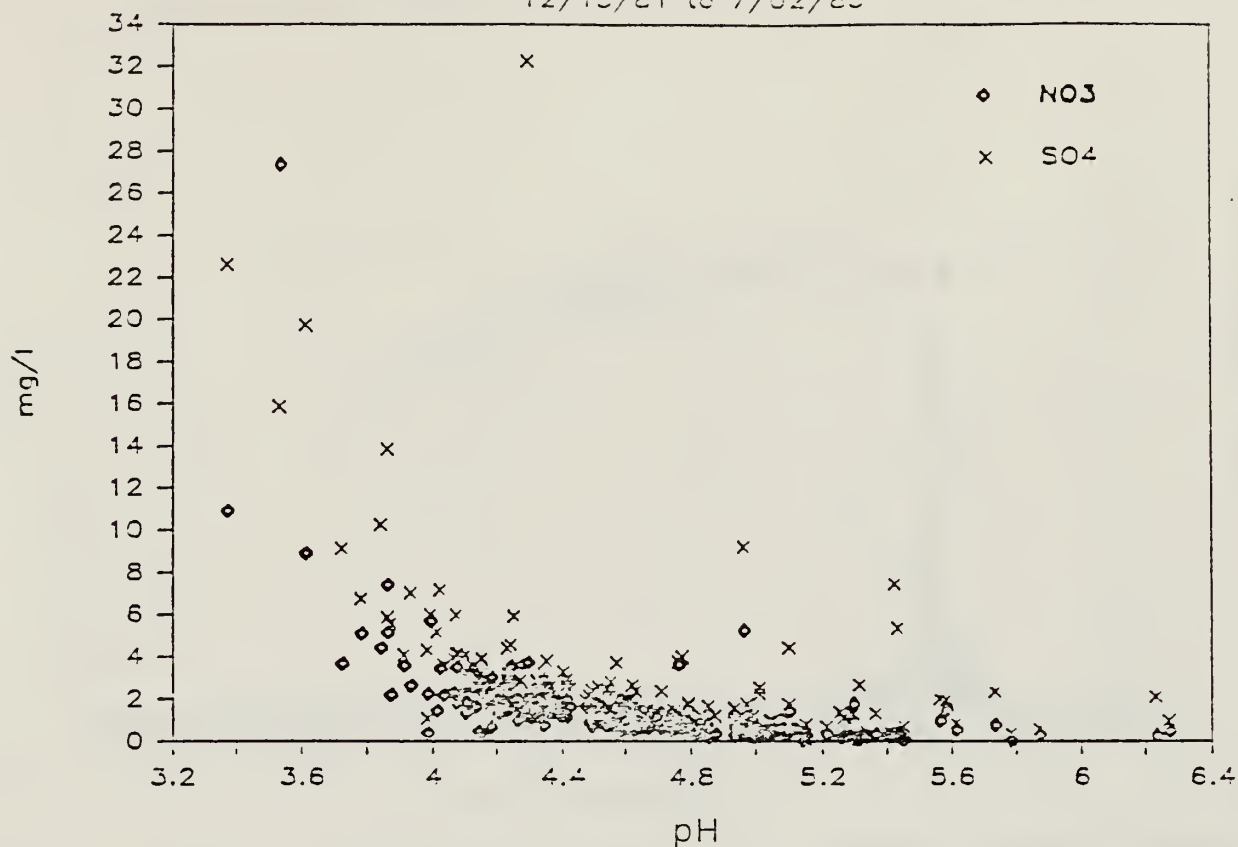
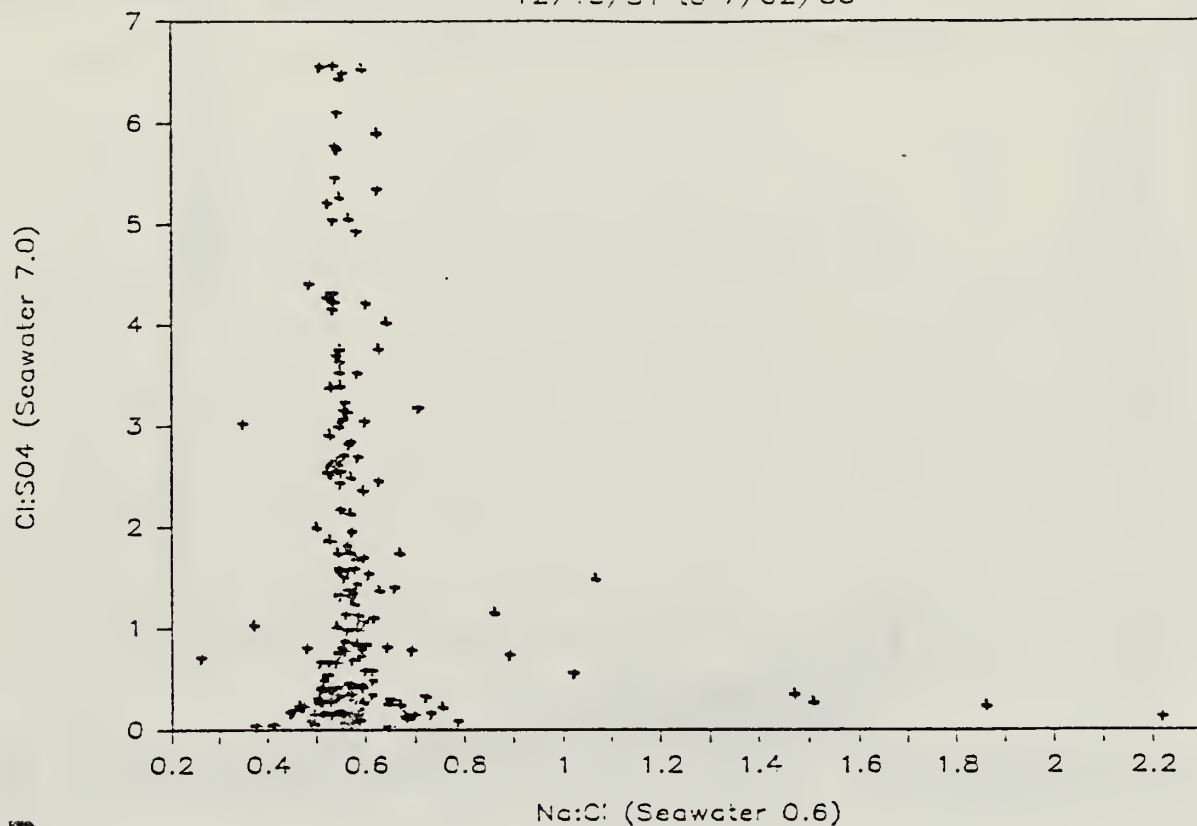


Fig. 27. Precipitation chemistry, Truro station, Outer Cape Cod. NO<sub>3</sub> + SO<sub>4</sub> v precipitation pH. Analysis done on a weekly basis by the NADP (National Acid Deposition Monitoring Program). Data provided by M. Foley and P. MacDonald, National Park Service, Boston.

A

## PRECIPITATION CHEMISTRY: OUTER CAPE COD

12/15/81 to 7/02/85



B

## PRECIPITATION CHEMISTRY: OUTER CAPE COD

12/15/81 to 7/02/85

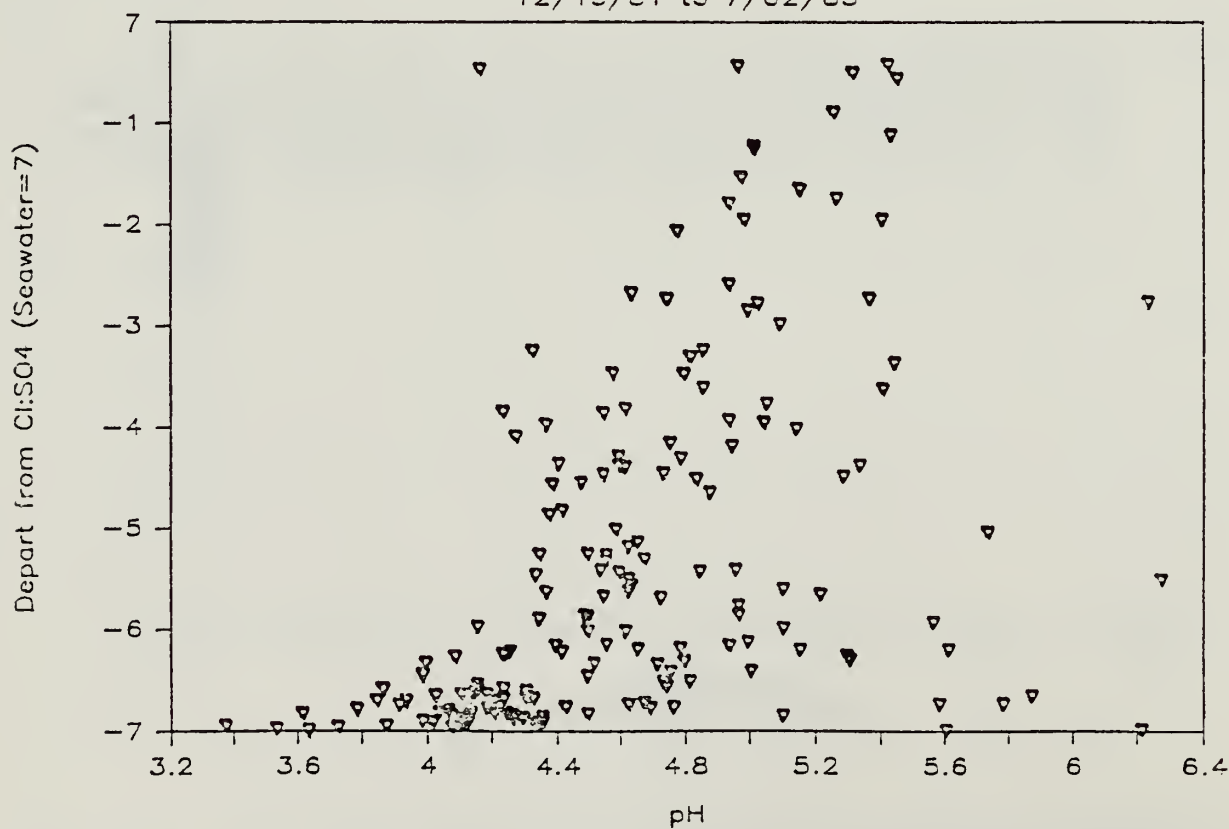


Fig. 28. Precipitation chemistry, Outer Cape Cod. A. Cl:SO<sub>4</sub> v Na:Cl  
B. Departure from Cl:SO<sub>4</sub> ratio of 7:1 v precipitation pH.

# PRECIPITATION CHEMISTRY

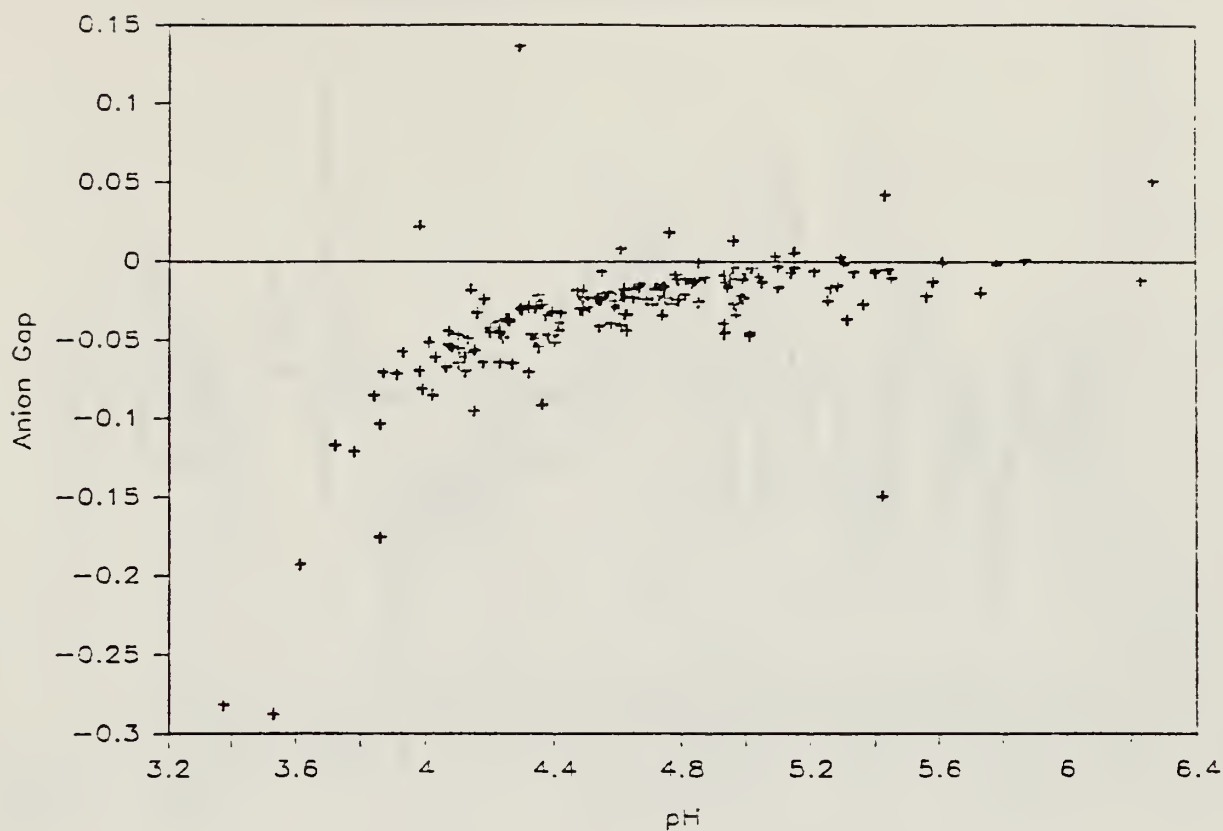


Fig. 29. Precipitation chemistry, Outer Cape Cod. Anion gap (difference in meq/l between the sum of cations and the sum of anions) plotted against precipitation pH.



## Precipitation pH: Outer Cape Cod

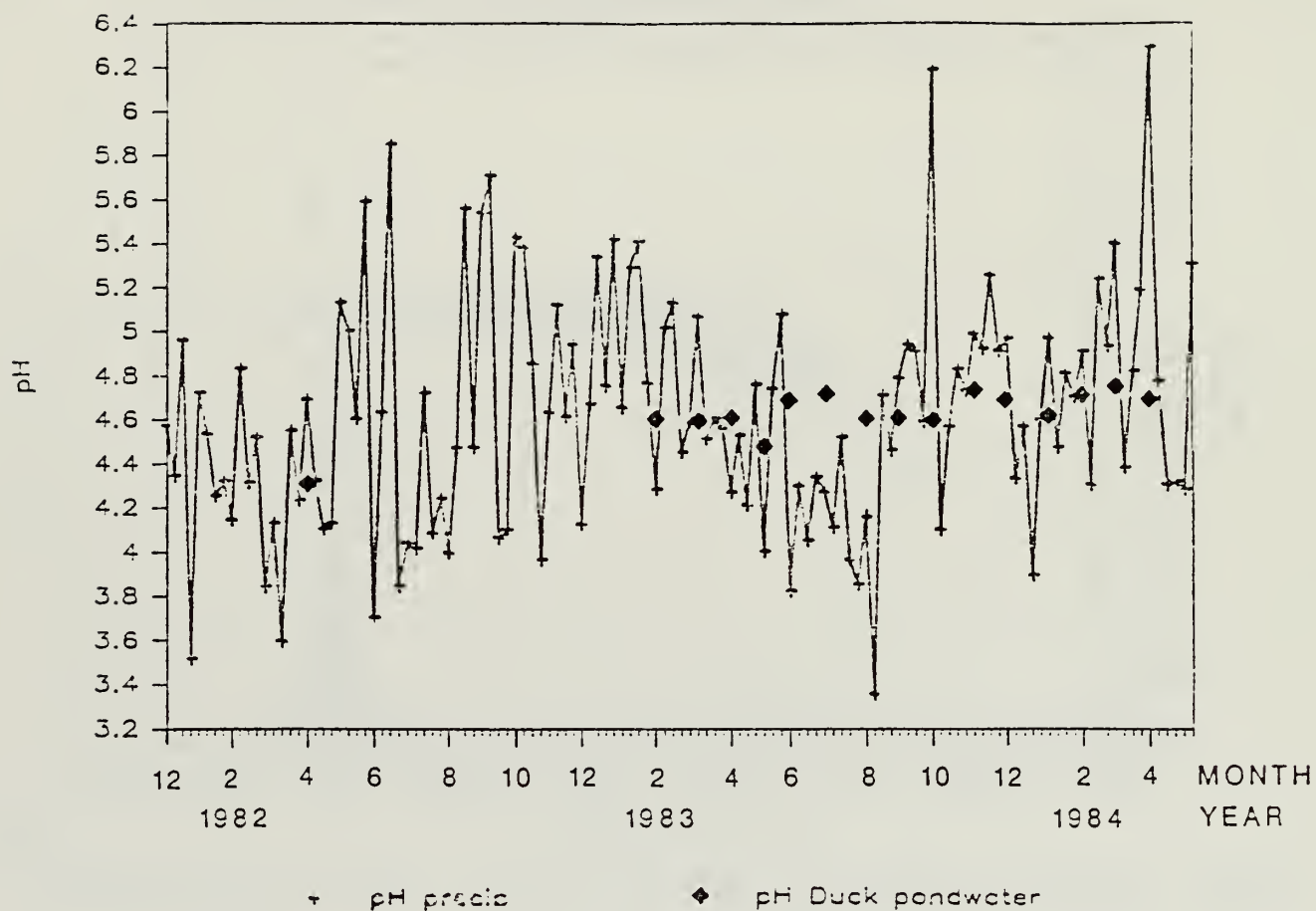


Fig. 30. Weekly readings of precipitation pH, Outer Cape Cod, for the period from 12/15/81 to 5/84. Observed pH values from Duck Pond, when taken during that time, are plotted on the same scale.

# PRECIPITATION CHEMISTRY: OUTER CAPE COD

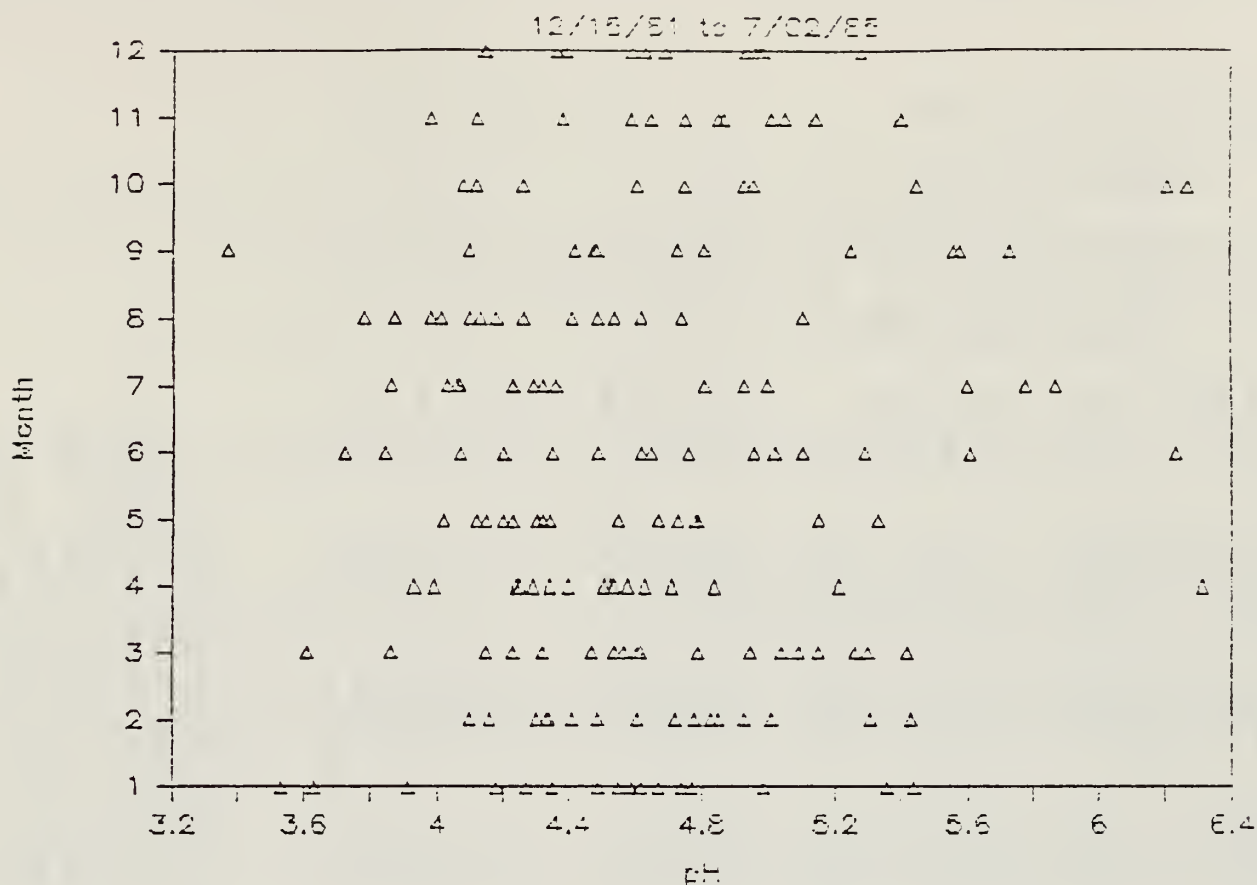


Fig. 31. Precipitation pH, Outer Cape Cod, plotted against month of occurrence. There is no discernible seasonal trend.

Mxd	ha	Plk	pH <sub>o</sub>	pH <sub>a</sub>	P	TP	NN	Na	Condu	Conda	Alk
Kinnareum	4.00	15.00	4.10	4.35	0.60	14.00	3.00		80.00	86.00	-10.25
Long	15.00	11.00	4.22	4.62				21.00	85.00	95.00	-7.50
Dyer	11.00	25.00	4.25	4.51	0.60	6.40	3.00	30.00	85.00	89.00	-1.25
Grease (W)	16.00	12.50	4.23	4.42	0.50	3.30	50.00	30.00	115.00	112.50	-1.60
Duck	18.00	39.00	4.32	4.61	0.60	6.40	4.00	0.70	97.00	106.00	-1.50
Grease (T)	11.00	45.00	5.00	6.03	1.20	14.00	7.00	0.80	130.00	127.00	1.25
Speccanale	7.00	49.00	5.00	4.94		11.00	5.00		110.00	123.00	-4.50
Gull	19.00	67.00	6.26	6.56	0.90	8.30	30.00	0.90	119.00	126.00	2.50
Herring, W	5.00	46.00	5.46	5.47	1.80	9.20	5.00	0.50	146.00	143.00	-4.00
Ryder	11.00	78.00	5.45	5.68				0.50	113.00	120.00	-4.00
Williams	2.00	41.00	5.00	5.50	1.20	27.00	6.00	0.90	122.00	99.00	-3.50
Herring, W	4.00	64.00	5.90	6.08	6.80			0.90	110.00	120.50	3.00
Herring, E	11.00	43.00	6.39	7.43	3.70			50.00	517.00	741.00	
Higgins	6.00	60.00	6.10	6.36	1.50	16.00	4.00	0.80	119.00	122.00	-0.75
Pilgrim	2.00	60.00	7.50	7.50	8.00			2.20	946.00		
	Cao	Can	Fe	Na	Cl	Cl <sub>o</sub>	Mg	K	Vol <sub>LI</sub>	S	
Kinnareum	0.80	0.80		11.00		1.50	1.59	1.00	3.20		
Long	1.59		12.00	12.90	21.20				225.00	6.29	
Dyer	1.40	1.00	20.00	11.70	24.90	0.70	1.50	0.80	52.00	6.00	
Grease (W)	1.50	1.10	12.00	15.40	32.00	0.90	2.00	1.00	284.80		
Duck	1.19	1.00	10.00	13.70	24.90	1.50	1.80	0.80	91.80	7.60	
Grease (T)	5.29	1.90	37.00	16.90	35.50	1.70	1.80	0.80	77.00	6.15	
Speccanale	1.00	1.00		17.00					3.50		
Gull	1.90	1.50	10.00	17.10	32.00	1.50	2.39	1.09	806.00	9.20	
Herring, W	1.59	1.60	20.00	24.00		2.30	2.00	1.30	50.00	10.10	
Ryder									91.30	5.75	
Williams	2.59		840.00	26.00	42.50	2.30	2.80	1.09	7.20	3.20	
Herring, W	2.00	1.20	125.00	17.50	42.50	7.90	2.30	1.00	32.40	6.80	
Herring, E	5.39	5.39	118.00	97.00	163.00	5.10	12.00	4.19	196.90	20.50	
Higgins	1.59	1.70	35.00	17.50	35.50	1.90	2.39	1.09	67.80	7.50	
Pilgrim	90.00	90.00	215.00	182.00	347.00	9.80	230.00	69.00	292.00		

Table 1. Morphometric and Chemical Data: Outer Cape Cod Ponds.

Mxd = maximum depth (m), ha = hectares, Plk = % plankton diatoms, pH<sub>o</sub> = 9/75 + 4/82 values, pH<sub>a</sub> = mean pH (all values), P = PO<sub>4</sub>-P, TP = total phosphorous, NN = Total nitrogen, nit = NO<sub>3</sub>-N, Condo = conductance (umhos/cm), 9/75 + 4/82 values, Conda = 1983 values, Alk = alkalinity, 4/82 values (mgCaCO<sub>3</sub>/l), Cao = calcium, 1975, Can = calcium, 1983, Fe = iron (ppb), Na = sodium (ppb), Cl = chloride (ppb), Cl<sub>o</sub> = chlorophyll a, Mg = magnesium (ppb), Amm = ammonia (NH<sub>4</sub>-N), K = potassium (ppb), Vol<sub>LI</sub> = volume index calculated by multiplying Mxd by ha, S = sulfate (ppb).





	A	B	C	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	
	Mxd	ha	Plk	PHo	Pha	p	TP	NN	Nlt	Condo	Condn	Alk	Cao	Can	Fe	Na	Cl	CIA	Mg	Amm	K	Voll	S	%Acb	%acp	%Ind	%alk	%AkB	%Ac	nAlk	%Cha	
#1	1 000	-192	-005	-299	-219	-612	-646	0 568	0 303	-317	-327	0 230	-355	-409	-564	-344	-465	-502	-412	-387	-412	-011	0 018	0 539	-049	-049	-429	-330	0 413			
#2	1 000	0 241	0 685	0 645	0 645	0 655	-220	0 630	-144	0 860	0 816	0 420	0 95	0 94	0 040	0 275	0 895	0 674	0 943	0 946	0 96	0 294	-155	-413	0 037	0 552	0 731	-354				
#3	1 000	0 654	0 64	0 479	0 64	0 479	0 414	-329	-617	0 257	0 210	0 543	0 283	0 552	0 050	0 272	0 268	0 421	0 255	0 156	0 254	-146	-615	-507	0 617	0 521	0 150	-65				
#4	1 000	0 95	0 719	0 480	0 95	0 719	0 480	-085	-226	0 725	0 455	0 645	0 635	0 632	0 073	0 72	0 732	0 714	0 630	0 611	0 631	0 492	-523	-376	0 446	0 954	0 683	-645	0 703	-849		
#5	1 000	0 676	0 496	0 663	1 000	0 676	0 496	-063	-052	0 715	0 664	0 665	0 526	0 530	0 125	0 714	0 694	0 994	0 714	0 706	0 714	0 659	-265	-671	0 255	0 704	0 645	-665	0 855	-828		
#6	1 000	0 903	-300	1 000	0 903	-300	1 000	-432	-510	0 119	0 140	0 230	0 216	0 587	0 94	0 125	0 351	0 657	0 484	-379	0 066	-313	-317	0 078	-684	0 276	0 508	-003	-534	-210	-567	
#7	1 000	0 465	0 117	0 066	0 172	-040	-113	-307	-029	0 004	-004	-256	0 231	-276	0 159	0 049	-104	-145	-019	-142	0 019	0 652	0 138	0 217	-364	-140	0 207	0 234	0 841	-195		
#8	1 000	0 123	0 66	-346	-155	-157	-195	0 128	0 069	-104	-145	-019	-142	0 019	0 652	0 138	0 217	-364	-140	0 207	0 234	0 841	-195	-544	0 024	0 688	0 93	538	0 915	-641		
#9	1 000	0 997	0 492	0 905	0 91	0 91	0 633	0 996	0 995	0 426	0 997	0 825	0 995	0 072	0 960	-212	-479	0 116	0 562	0 953	478	0 917	-604	0 440	0 476	0 100	-551	0 832	-604			
#10	1 000	0 450	0 695	1 000	0 995	0 133	0 90	0 931	0 730	0 999	0 98	0 999	0 98	0 999	0 177	0 560	-145	-424	0 036	0 543	0 775	-403	0 746	-701	0 555	0 789	-432	0 931	-727			
#11	1 000	0 80	0 910	0 933	0 730	1 000	0 996	1 00	0 174	0 935	-126	-454	0 016	0 555	0 789	-432	0 931	-727	0 555	0 789	-432	0 931	-727	0 555	0 789	-432	0 931	-727	0 555	0 789		

Table 3. Correlation matrix of morphometric, chemical, and diatom pH group variables: Outer Cape Ponds. Abbreviations as listed in Table 1. caption and Figure 10 caption.

\*\*\*\*\*  
 \* Regression Coefficients \*  
 \*\*\*\*\*

Variable	Coefficient	Std Error	t(2-Tailed)
Constant	2.474940		
% Acidbionts	1.725880E-02	.4524408	3.813837E-02
% Acidophils	2.270139E-02	.4524480	5.035131E-02
% Indifferent	4.146734E-02	.4524400	9.165091E-02
% Alkaliphils	4.613873E-02	.4524408	.1019756
% Alkibionts	.3492483	.4524488	.7719068

\*\*\*\*\*  
 \* Regression Statistics \*  
 \*\*\*\*\*

Number of Independent Variables = 5  
 Number of Cases = 14  
 Number of Cases with Missing Data = 0  
 Coefficient of Determination (R<sup>2</sup>) = .0060595  
 Coefficient of Multiple Correlation (R) = .9413068  
 Standard Error of Estimate (SEE) = .4524488  
 F-ratio (F) = 7.776436  
 Degrees of Freedom (df)  
     Regression (numerator) = 5  
     Residuals (denominator) = 8

\*\*\*\*\*  
 \* Regression Estimates \*  
 \*\*\*\*\*

Case #	plla	Regr Estimates	(0-C) Residuals
1	4.35	4.339474	.0105257
2	4.62	4.644075	-2.407503E-02
3	4.51	4.792799	-.2827993
4	4.49	4.795490	-.3054977
5	6.03	5.70417	.3258295
6	4.94	4.805456	.1345444
7	6.56	5.64491	.9150901
8	5.47	5.611705	-.141705
9	5.68	6.026034	-.3460336
10	5.5	5.877033	-.3770332
11	6.08	5.860631	.2193694
12	7.48	7.198902	.2830973
13	6.36	6.505401	-.145401
14	7.5	7.765928	-.2659278

### Regression Variables

	plla	%Acb	%acp	%Ind	%alk	%alk	%lac
Pinnaeus	4.35	40.00	51.00	0.30	0.00	0.00	91.00
Long	4.62	33.00	45.00	6.40	6.70	0.00	78.00
Oyer	4.51	1.60	71.00	15.00	1.10	0.00	73.00
Great(W)	4.49	0.55	67.22	8.90	8.90	0.00	68.00
Great(I)	6.03	2.60	42.00	24.00	23.00	0.49	44.60
Spectacle	4.94	2.10	70.97	4.23	6.34	0.60	73.00
Cull	6.56	0.00	38.00	23.00	27.00	0.30	30.00
Horseleech	5.47	0.02	31.00	23.00	32.00	0.00	31.00
Ryder	5.68	0.00	29.00	43.00	24.00	0.00	29.00
Williams	5.50	0.00	17.00	22.00	38.00	1.00	17.00
Herring(W)	6.08	0.00	15.00	23.00	45.00	0.04	15.00
Herring(I)	7.48	0.00	7.00	19.00	64.40	2.30	7.00
Illegins	6.36	0.00	4.00	16.00	71.00	0.00	4.00
Fulgria	7.50	0.50	2.63	15.00	77.00	3.00	3.00

Table 4. Regression coefficients, statistics, estimates, and variables used to reconstruct past pH values in this study.

Table 5. Synthesis of pollen, charcoal, vegetation, and climate data from Duck Pond Core D stratigraphy (Winkler, 1985a).

Pollen Zone	Approx. Age (yr B. P.)	Total PDR (x 10 <sup>3</sup> ) (g/cm <sup>2</sup> /yr)	$\bar{x}$ CDR	$\bar{x}$ % C	Climate	Vegetation	Plant Community
3e	330-present	13.0-23.9	0.0104	5.4	cooler-wetter	Pitch pine-oak	European settlement changes
3d	2200-330	10.0-3.0	0.0042	4.8	cooler-wetter	Pitch pine-oak-white pine	More mesophytic
3c	5000-2200	7.1-12.5	0.0022	4.4	less warm-less dry	Pitch pine-oak-white pine	Pine barrens-trans. to more mesophytic
3b	8200-5000	26.3-10.3	0.0029	4.5	warmer-drier	Pitch pine-oak	Pine barrens
3a	9000-8200	131.2-50.2	0.0084	5.6	warmer-drier	Pitch pine-oak-hemlock-beech-hickory	Mixed mesophytic forest-transition to pine barrens
2b	9500-9000	31.6-33.5			warm-wet	White pine-pitch pine-hemlock-oak-beech-ironwood	Mixed mesophytic forest
2a	9800-9500	26.5-28.9	0.0044	4.6	warmer-wet	White pine-jack pine	Northern conifer
1c	10,500-9800	14.0-28.7			cool-wet	White pine-jack pine-spruce-green alder	Boreal forest trans. to northern conifer
1b	11,500-10,500	7.7-14.9	0.0009	1.8	cool-dry	Spruce-jack pine-green alder	Boreal forest
1a	12,000-11,500	1.9-3.4			cold-dry	Spruce-Hudsonia-grass	Tundra-spruce parkland

A

	RHB	mlrPH	PHAc	PHCB	Depth	Clnfl	hPine	dPine	TPine	Char	Peri	Acb	acp	Ind	Alk	Alkb	TAcid	Mdis	Ftot	Cycc	Cyccs	Tabt
1	1.000	0.601	0.638	1.000	-0.332	0.262	0.318	-0.220	0.056	-0.100	0.048	-0.105	-0.621	0.346	0.538	0.371	-0.636	-0.534	0.449	0.308	0.228	0.048
2	1.000	1.000	0.348	0.603	0.098	-0.041	0.220	-0.585**	-0.347	-0.343	-0.153	-0.303	-0.301	0.175	0.546**	0.357	-0.346	-0.166	0.309	0.166	0.028	0.017
3		1.000	1.000	0.642	-0.237	0.114	0.134	-0.301	-0.042	-0.105	0.216	-0.065	-0.991	0.807	0.414	-0.309	-1.000	-0.544	0.262	0.742	0.648	-0.329
4			1.000	-0.329	1.000	-0.525	-0.102	-0.106	-0.300	-0.106	0.047	-0.106	-0.620	0.350	0.540	0.367	-0.640	-0.536	0.450	0.313	0.231	0.049
5				1.000	1.000	-0.222	0.100	-0.108	0.400**	0.146	-0.005	-0.415**	-0.104	0.391	-0.324	0.283	-0.133	-0.338	-0.287	0.353	0.260	0.369
6						1.000	1.000	1.000	0.015**	0.295	0.425	0.336	0.236	-0.207	-0.252	-0.160	0.300	-0.241	-0.135	-0.315	-0.233	0.257
7							1.000	1.000	1.000	0.352	0.172	0.106	0.021	0.086	-0.311	0.052	0.043	-0.357	-0.220	0.009	0.034	0.370
8								1.000	1.000	1.000	-0.244	0.036	0.056	-0.126	-0.082	-0.027	0.102	0.316	0.193	0.004	-0.225	-0.173
9									1.000	1.000	1.000	0.099	-0.237	0.155	0.102	-0.400	-0.214	-0.577**	0.043	-0.000	0.046	-0.041
10										1.000	1.000	1.000	-0.011	-0.202	0.106	-0.210	0.067	0.041	0.258	-0.276	-0.039	-0.170
11											1.000	1.000	1.000	-0.802**	-0.415	0.347	0.991**	0.554**	-0.203	-0.737**	-0.650**	0.350
12												1.000	1.000	1.000	-0.160	-0.279	-0.008**	-0.502**	-0.295	0.092**	0.000**	-0.217
13													1.000	1.000	1.000	1.000	-0.101	-0.157	0.924**	-0.112	-0.276	-0.186
14														1.000	1.000	1.000	1.000	0.311	0.194	-0.052	-0.191	0.217
15															1.000	1.000	1.000	0.543**	-0.260	-0.744**	-0.647**	0.339
16																1.000	1.000	1.000	-0.064	-0.345	-0.501	-0.445**
17																	1.000	1.000	1.000	0.740**	-0.254	
18																		1.000	1.000	1.000	1.000	
19																			1.000	1.000	1.000	
20																				1.000	1.000	
21																					1.000	
22																						1.000

\*\*d=0.005

\*\*p=0.005

\*p=0.01

B

	Acb	acp	Ind	alk	Akb	EunU	Plank	Peri	TAc	Amb	Char
1	1.000	-0.348	-0.133	-0.324	-0.304	0.133	-0.900**	0.900**	0.190	0.438	0.164
2	1.000	1.000	-0.481	-0.650**	0.357	-0.345	0.297	-0.297	0.037**	-0.632	0.565
3		1.000	1.000	0.476	-0.393	0.046	0.179	-0.179	-0.590	0.491	-0.629*
4			1.000	1.000	-0.094	0.159	0.362	-0.362	-0.863**	0.239	-0.472
5				1.000	1.000	-0.271	0.241	-0.241	0.171	-0.920	0.623*
6						1.000	-0.317	0.317	-0.103	0.272	0.000
7							1.000	-1.000**	-0.228	-0.334	-0.179
8								1.000	0.229	0.384	0.179
9									1.000	-0.372	0.703**
10										1.000	-0.629
11											1.000

Table 6. Correlation matrices of pollen, charcoal, and diatom percentages.

A. Duck Pond Core D: 12,000-year record.

B. Core DD: post-European-settlement.

Relavant abreviations are: A: hPine = %

haploxylon pine pollen, dPine = % diploxylon

pine pollen, TPine = % total Pine pollen,

CInfl = charcoal influx, Peri = % periphytic

diatoms, TAcid = % total acid diatoms, Mdis =

% Melosira distans, Ftot = % total Fragilaria,

Cycc = % Cyclotella comta, Cyccs = % C. stelligera,

Tabt = % total Tablellaria; in B: EunU = %

unspecified Eunotia, Amb = % Ambrosia pollen,

and Char = % charcoal.



Table 7. Reconstructed pH history of Duck Pond, S. Wellfleet, Massachusetts. The mean pH (and standard deviation) of each pollen zone is calculated. The regression equation has an  $r^2$  of 0.89 and a standard error of the estimated pH of  $\pm 0.45$ .

<u>Time (yr B. P.)</u>	<u>Pollen Zone</u>	<u>mean pH (mlr w Akb)</u>	<u>mean pH (mlr w/o Akb)*</u>
150 - present	3e2	4.96 $\pm$ 0.08	4.95 $\pm$ 0.08
330 - 150	3e1	5.25 $\pm$ 0.17	5.23 $\pm$ 0.2
2200 - 330	3d	5.37 $\pm$ 0.43	5.02 $\pm$ 0.23
5000 - 2200	3c	5.6 $\pm$ 0.09	5.6 $\pm$ 0.09
8000 - 5000	3b	5.19 $\pm$ 0.23	5.1 $\pm$ 0.12
9000 - 8000	3a	5.46 $\pm$ 0.12	5.46 $\pm$ 0.12
10500 - 9000	2	4.97 $\pm$ 0.08	4.97 $\pm$ 0.08
11800 - 10500	1cb	5.41 $\pm$ 0.42	5.41 $\pm$ 0.42
before 12000	1a	4.83	4.83
middle Holocene	3a-3d	5.38 $\pm$ 0.3	5.24 $\pm$ 0.28
150 - present	3e2	4.96 $\pm$ 0.08	4.95 $\pm$ 0.08
12000 - 150		5.29 $\pm$ 0.29	5.2 $\pm$ 0.27
12000 - present	(overall mean)	5.23 $\pm$ 0.29	5.15 $\pm$ 0.27

\*This version of the equation was used in plotting Figures

Part II.

COMPARISON OF TWO ESTUARIES: HERRING RIVER IN WELLFLEET,  
AND PAMET RIVER IN TRURO

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# ABSTRACT

## TWO ESTUARIES IN THE CAPE COD NATIONAL SEASHORE: DIATOM DOCUMENTATION OF LAND-USE DIFFERENCES

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Diatom analysis of sediments taken from the Herring and Pamet River basins in the Cape Cod National Seashore in Massachusetts contrast the recent land-use history of these estuarine environments. Herring River in Wellfleet has been extensively ditched, drained, and diked both for mosquito control and for development. The sediments were sampled from this river in 1982 after an episode where low pH of about 3 was measured at many sites in the river basin. The dominant diatom in these sediments, Eunotia exigua, reflects this low pH episode, which was probably caused by sudden flushing of the decomposed salt-marsh peat from the spoil piles along the ditches. The sample taken from the portion of the Herring River which drains from the Gull-Higgins-Williams-Herring Pond complex, had diatoms more representative of the pond diatom flora, than of the impacted stretch of river below. Sediments taken from the main channel of the river where tidal influence is still present, had more of a balance between freshwater and brackish diatom assemblages. Diatom scrapings from a dead alewife found upriver, showed that the fish had been in the ponds at the head of the river and was on its journey back to the sea when it died (probably because of the very acid water in the river channel at the time).

The Pamet River basin in Truro has had less recent manipulation and the sediments contain a very diverse diatom flora. There is indication of some acid drainage coming from the Cranberry Bog near the head of the river (a slightly more acid diatom flora was found in the sediments collected below this site), but most of the diatoms in the sediments of the Pamet drainage basin are from a wide range of both freshwater and brackish species.



## INTRODUCTION

Diatom analysis of sediments taken from the Herring and Pamet River basins in the Cape Cod National Seashore in Massachusetts (Fig. 1) contrast the recent land-use history of these estuarine environments. Herring River in Wellfleet has been extensively ditched, drained, and diked both for mosquito control (Portnoy, 1984) and for development. Very little tidal water reaches inland most of the year, although alewives run upriver in the spring to spawn in the freshwater ponds which are the source of the river. The sediments were sampled from this river in June, 1982 after an episode where low pH of about 3 was measured at many sites in the river basin (Fig. 2). The pH was still low at the time the samples were taken for diatom analysis and the diatoms in the water, on plants, and in the sediments reflect this low pH episode (Figs. 3,4).

## METHODS

Sediments, water, plant, and fish scraping samples from the river basins were prepared for diatom analysis by treatment with  $H_2O_2$  and potassium dichromate (van der Werff, 1955). Strewn mounts were then prepared according to procedures in Patrick and Reimer (1966). Permanent slides were made with Hyrax mountant, Refractive Index 1.7. The slides were counted under oil immersion at 1000 x magnification; a total of about 400 valves was counted for each level. Diatoms were identified using floras compiled by Hustedt (1930, 1939, 1955), Boyer (1916), Huber-Pestalozzi (1942), Patrick and Reimer (1966, 1975), Foged (1980), Florin (1980), Koppen (1975), Germain (1981), Gasse (1980), Gasse *et al.*, (1983a), Gasse and Tekaiia (1983b); Camburn and Kingston (1985), and PIRLA (1985).

## RESULTS AND DISCUSSION

A diatom percentage diagram from the Herring River basin and the ponds which flow into the Herring River (H in Fig. 1) is presented in Figure 3. The dominant diatom in the sediments from streams adjacent to spoil piles (sites

1B, 2, 2S, 3, 6A, 7C, 9) was Eunotia exigua, an acidobiontic diatom tolerant of extremely acid water (van Dam et al., 1980; Kingston, 1982; Merilainen, 1967; Charles, 1985). It is found in monotypic abundance in the leachate from mining spoils and is also often the only diatom present in the most acid Sphagnum bogs (van Dam et al., 1980). Eunotia exigua was at times accompanied by Pinnularia subcapitata cf y hilseana, but in most of the samples it was present by itself in the thousands in one traverse of the slide. Sediments taken from the main channel of the river where some tidal influence was still maintained (site 3A), had more of a balance between freshwater and brackish diatom assemblages. Diatom scrapings from a dead alewife found upriver (site 7), showed that the fish had been in the oligotrophic ponds at the head of the river and was on its journey back to the sea when it died (probably because of the very acid water in the river channel at the time). The sample taken from site 11 had diatoms more representative of the pond diatom flora (described in detail in Part I. of this report), and the sample taken from site 4 had an alkaline estuarine flora more diverse than those from the impacted stretch of river below. The sample from site 6C, a small marsh near the bay but separate from the river, also had a more diverse diatom flora.

The Pamet River basin in Truro (P in Fig. 1) has had less recent manipulation. A diatom percentage diagram comparing both the Pamet River diatom flora with that of the Herring River is presented in Figure 4. The diatoms in the sediments throughout the drainage basin have a wide range of both freshwater and brackish species although there is an indication of some acid drainage coming from the Cranberry Bog near site 4 in the river (an increase in Eunotia species was found in the sediments collected below this site). The river maintains a fairly stable pH of about 6.5 (it's drainage basin, similar to the kettle ponds, is entirely in crystalline, non-calcareous outwash sands), and has conductance of about 570 umhos/cm except at high tide

when conductance increases to more than 1100 umhos/cm. It is possible that ditching in the Pamet River basin ended decades ago and acid leachate from decaying saltmarsh peat has long since been flushed out of the river basin.

In total there were more than 229 diatom species found in both rivers. Herring River had a total of 95 species (mainly because of the diversity of diatoms in sites 11, 4, 7, and 6C (Fig. 3,4; as noted above) (Appendix A). Pamet River had more than 169 species and only 35 of the same species were found in both river basins (Appendix B). Brackish species found in abundance in some of the Pamet River samples included several Amphora spp., Melosira jurgensis and M. nummuloides, Navicula halophila and varieties, N. elegans, N. hungarica, N. pygmaea, N. salinarum, and many Nitzschia and Synedra (esp. S. pulchella, rumpens, and r. v fragiloides) species. Plagiotropis, Pleurosigma, Gyrosigma, and Entomoneis spp. were also common. Several sites in the Pamet River basin had abundant diatoms indicative of eutrophic conditions such Diatoma elongatum and Fragilaria capucina (Fig. 4) suggesting that there may be a source of polluted drainage entering the basin.

#### CONCLUSION

Diatoms are very responsive to land-use changes and can be used to monitor the impacts of these changes. The rate of recovery from disturbance can also be monitored by analyzing the diatom assemblages in recent sediments (Fritz and Carlson, 1982). Comparison with relatively unimpacted regions is necessary to provide baseline assemblages unless longer pre-disturbance sediment cores are readily available.

If increased tidal water was present in the Herring River basin in the spring of 1982, the extremely acid leachate from the decomposition of the saltmarsh peat would have been diluted and effects from this kind of drainage would have been minimized. Current water management in the Herring River basin not only leads to increased abundance of the nuisance salt marsh

mosquito Aedes cantator (Portnoy, 1984), but contributes to seasonal extremes in pH in the river that causes fish (and probably amphibian) die-off, pollution of river water, and a dramatic decrease in river diatom flora. Continued ditching may affect the water quality in the Gull-Higgins-Herring pond complex, as well.

Seasonal sampling of diatoms from both the river basins will provide knowledge of the extent of variation of diatom species in the rivers and may signal pollution problems in the Pamet River basin before they become overwhelming.



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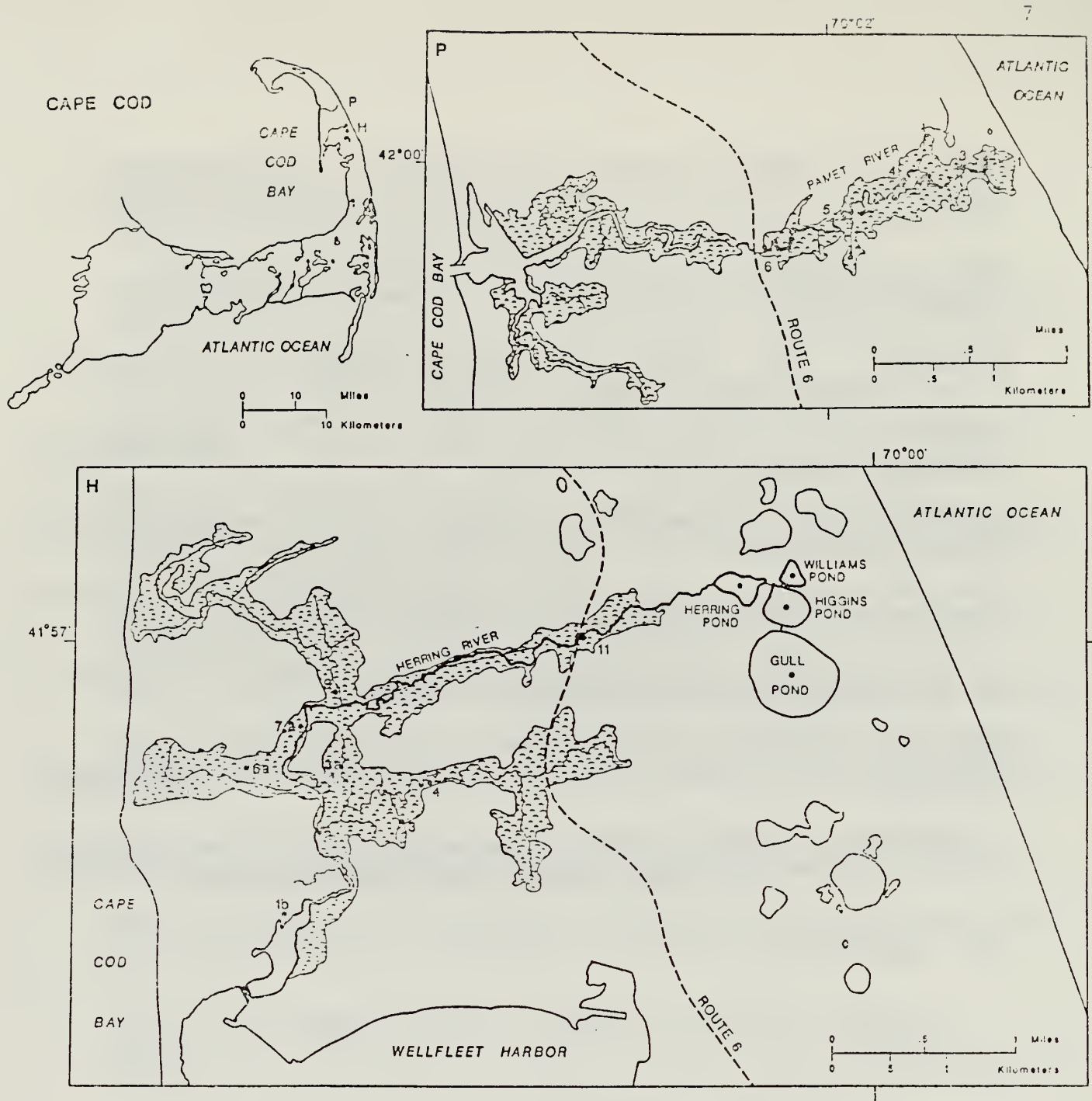
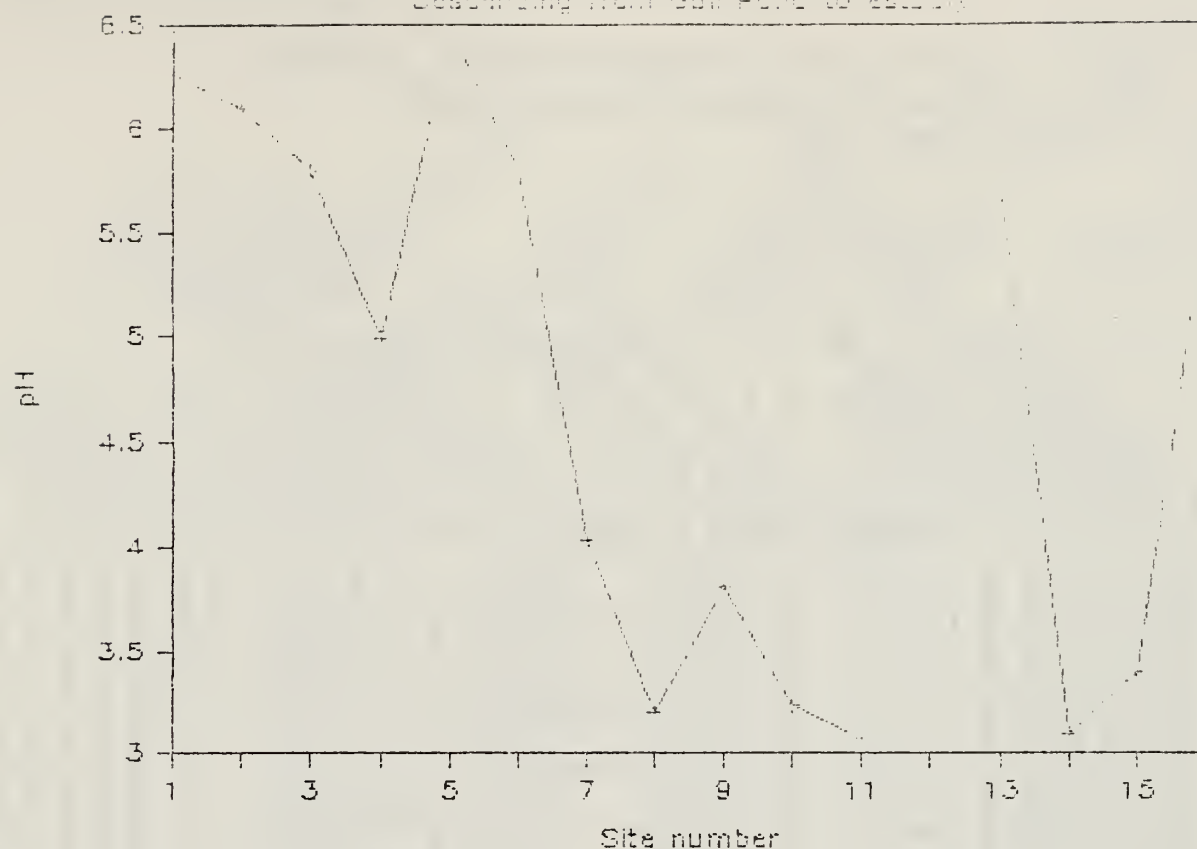


Fig. 1. Map of Cape Cod and the Herring (H) and Pamet Rivers (P) on the Outer Cape. P. Pamet River basin in Truro, Massachusetts. H. Herring River basin in Wellfleet, Massachusetts.

# Herring River Drainage Basin

8

Descending from Gull Pond to estuary



# Herring River Drainage Basin

Descending from Gull Pond to estuary

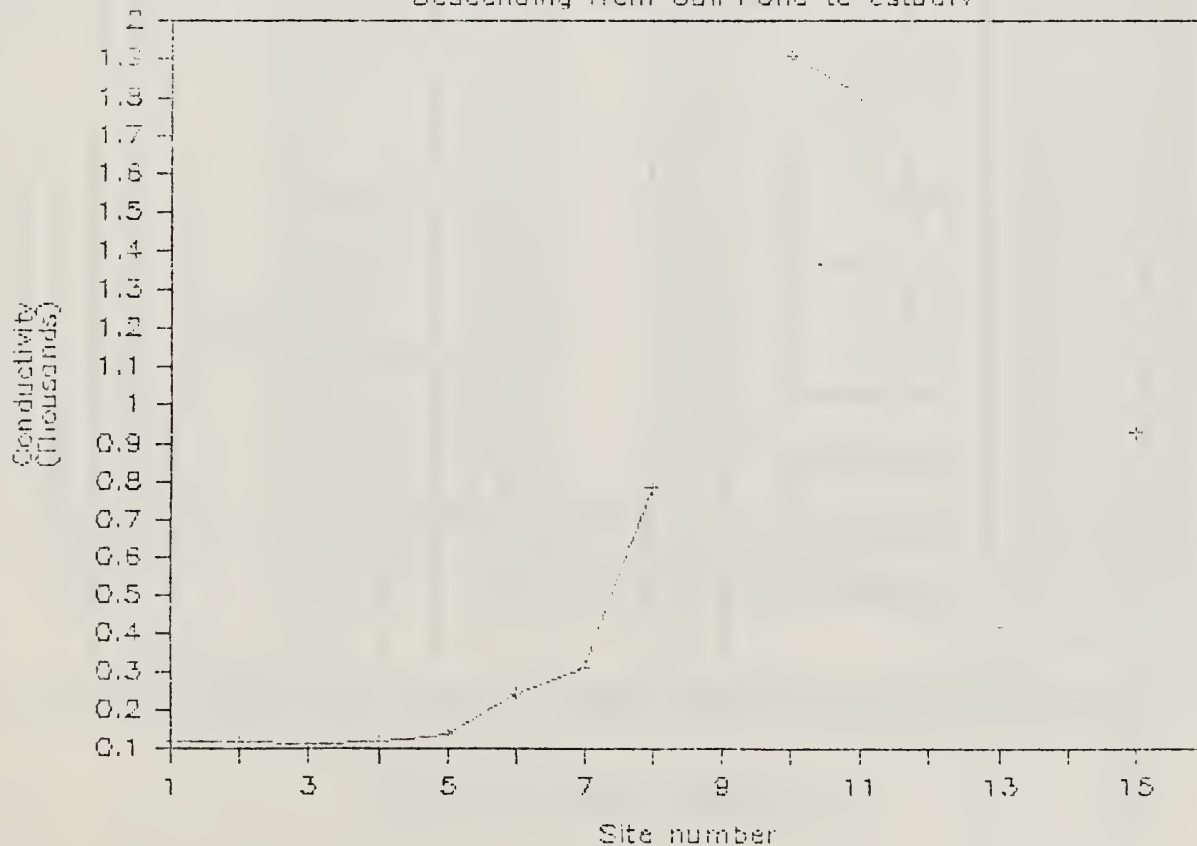


Fig. 2. pH measured June 11, 1982 at sites in the Herring River drainage basin. Conductance measured at the same time. pH and conductance of the ponds are mean values (see Part I). Sites 1, 2, 3, and 4 are Gull, Higgins, Herring, and Williams Ponds.



# Herring River

Gull, Higgins, Herring, and Williams Ponds, Wellfleet  
Cape Cod National Seashore, Massachusetts  
Diatom Percentages 1985

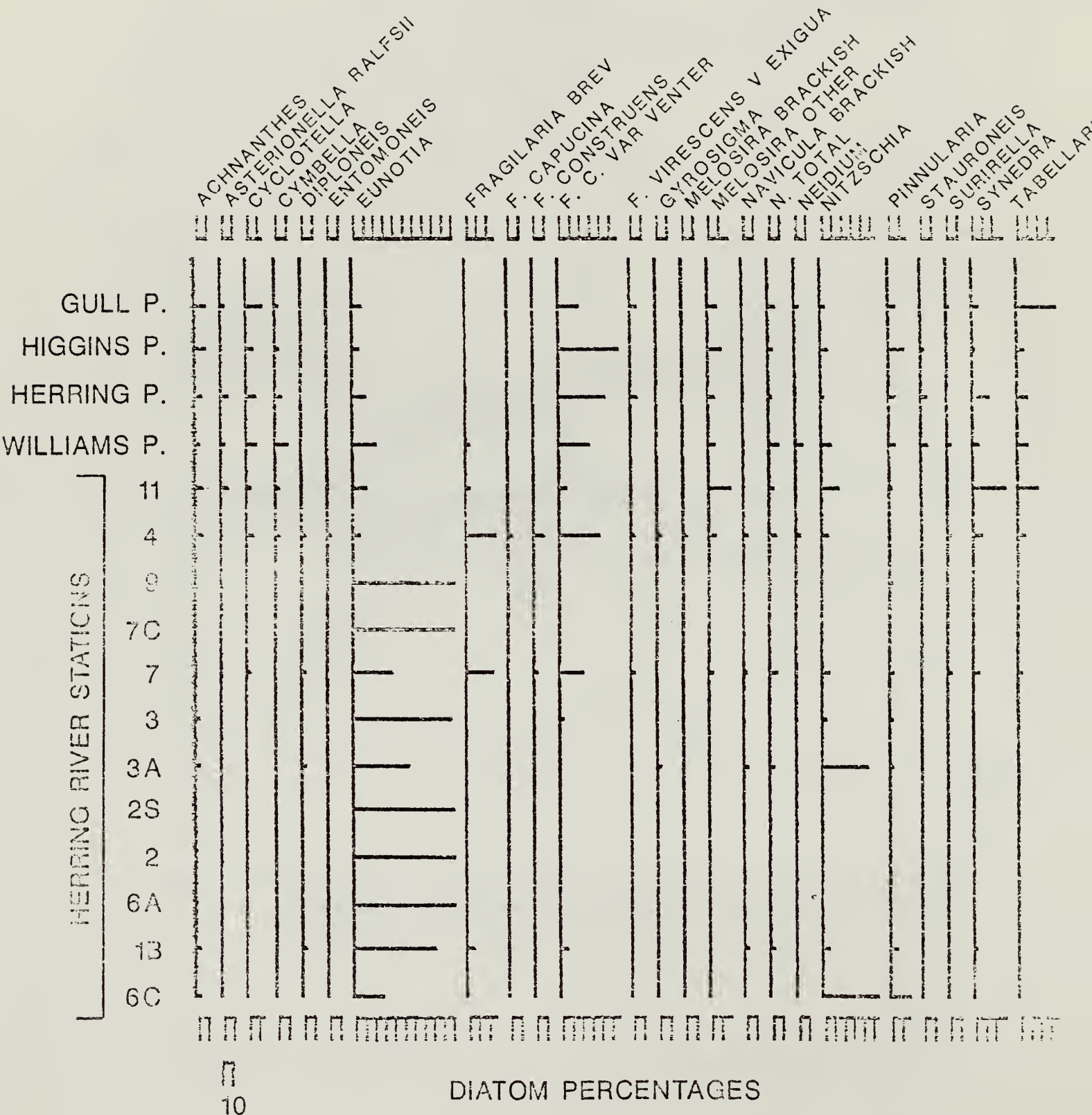


Fig. 3. Diatom percentage diagram: Gull-Higgins-Herring-Williams ponds and sites in the Herring River drainage basin.

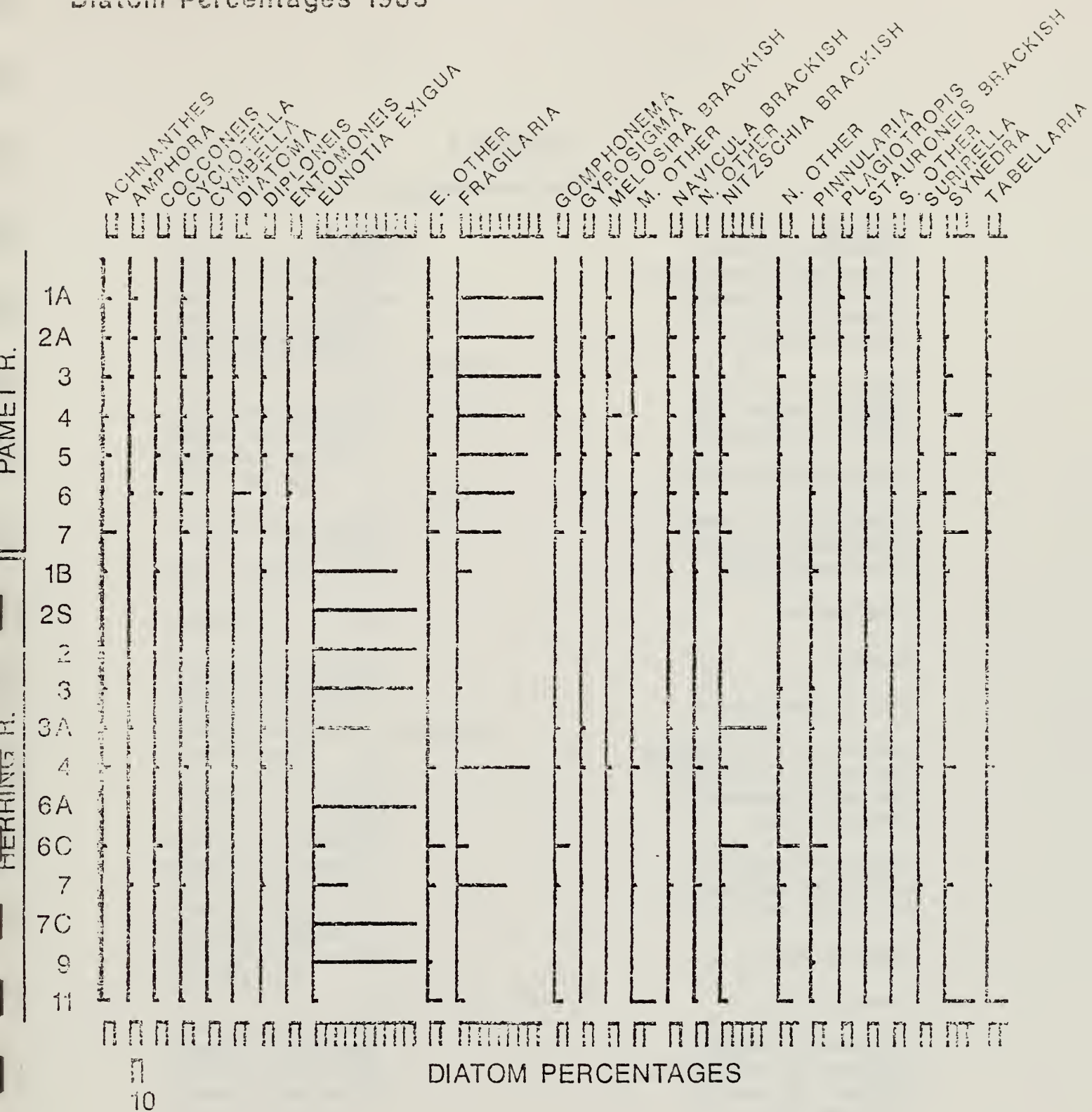


Fig. 4. Diatom percentage diagram: Pamet River basin and sites in the Herring River basin.

APPENDIX A

## HERRING RIVER DIATOMS

<u>Species</u>	<u>Site #</u>
Achnanthes deflexa	4
Achnanthes cf delicatula	1b, 6C
Achnanthes flexella	11
Achnanthes hungarica	11
Achnanthes spp.	3, 3A, 4, 11
Amphora cf granulata	7
Amphora ovalis type	3A
Amphora subangularis	7
Anorthoneis eurystoma	7
Asterionella formosa	11
Asterionella cf ralfsii	11
Asterionella spp	7
Brebissonia	1b
Caloneis	7
Chrysophyte cysts	7
Cocconeis cf latestriata	1b
Cocconeis cf scutellum	1b
Cocconeis placentula	11
Cocconeis spp.	6C, 7
Cyclotella comta	7, 11
Cyclotella menenghiana	11
Cyclotella spp.	11
Cymbella spp.	11
Desmogonium cf	11
Diploneis cf didyma	3A
Diploneis cf ostracodarum	1b
Diploneis cf vetula	7
Diploneis spp.	7
Eunotia alpina	7, 11
Eunotia carolina	4
Eunotia curvata	4
Eunotia curvata v capitata	9
Eunotia elegans	11
Eunotia exigua	1b, 2 Sfc, 2, 3, 3A, 4, 6A, 6C, 7, 7C, 9, 11
Eunotia incisa	4, 6C, 7, 11
Eunotia naegeli	4
Eunotia pectinalis	11
Eunotia pectinalis v minor	11

<i>Eunotia tenella</i>	7, 11
<i>Eunotia vanheurckii</i>	4, 6C
<i>Eunotia vanheurckii</i> v <i>intermedia</i>	11
<i>Eunotia</i> spp.	4, 6C, 11
<i>Fragilaria brevistriata</i>	1b, 4, 7, 11
<i>Fragilaria construens</i>	3, 4, 7
<i>Fragilaria construens</i> v <i>venter</i>	1b, 4, 7, 11
<i>Fragilaria lapponica</i>	7
<i>Fragilaria pinnata</i>	4, 7, 11
<i>Fragilaria virescens</i> v <i>exigua</i>	4, 7
<i>Gomphonema acuminatum</i> v <i>clavus</i>	11
<i>Gomphonema affine</i>	11
<i>Gomphonema gracile</i>	11
<i>Gomphonema</i> spp.	3A, 4, 6C, 7, 11
<i>Hantzschia amphioxus</i>	6C
Marine diatoms	3, 3A, 9
<i>Mastogloia</i>	7
<i>Melosira</i> cf <i>ambigua</i>	11
<i>Melosira</i> cf <i>distanis</i>	4
<i>Melosira italica</i>	4, 7, 11
<i>Melosira italica</i> v <i>tenuissima</i>	11
<i>Melosira</i> spp.	4
<i>Meridion circulare</i>	4, 7, 11
<i>Navicula brehemensis</i>	4, 11
<i>Navicula</i> cf <i>lyra</i>	1b, 3A, 7
<i>Navicula minima</i>	4
<i>Navicula pupula</i>	7, 11
<i>Navicula pygmaea</i>	7
<i>Navicula radiosa</i> type	4, 7
<i>Navicula</i> spp.	7, 11
<i>Nitzschia</i> cf <i>acuta</i>	7
<i>Nitzschia dissipata</i>	3A, 4, 7, 11
<i>Nitzschia palea</i>	3, 6C, 11
<i>Nitzschia perpusilla</i>	11
<i>Nitzschia pusilla</i>	1b, 3A, 4, 6C
<i>Nitzschia recta</i>	1b, 3A, 6C
<i>Nitzschia scalaris</i>	4, 11
<i>Nitzschia</i> spp.	6C, 7
<i>Pinnularia microstauron</i>	4
<i>Pinnularia stomatophora</i>	11
<i>Pinnularia subcapitata</i>	1b, 3, 3A, 4, 6C, 7, 9
<i>Pinnularia</i> spp.	3, 3A, 11
<i>Plagiogramma rhombicum</i>	3A



Pleurosigma	3A
Stauroneis cf kreigeri	4
Surirella ovulum	7
Synedra fasciculata	4
Synedra cf mazamaensis	7
Synedra rumpens	7, 11
Synedra rumpens v fragiloides	4, 7, 11
Synedra ulna	4, 7, 11
Synedra vaucheriae	11
Synedra spp.	1b, 4, 7, 11
Tabellaria fenestrata	11
Tabellaria flocculosa	4, 7
Tabellaria flocc. v linearis	11

APPENDIX B.

## PAMET RIVER DIATOMS

<u>Species</u>	<u>Site #</u>
<i>Achnanthes affinis</i>	1A
<i>Achnanthes clevei</i>	2A
<i>Achnanthes deflexa</i>	3, 4
<i>Achnanthes delicatula</i>	2A, 7
<i>Achnanthes lanceolata</i> v <i>rostrata</i>	2A, 4
<i>Achnanthes</i> cf <i>saxonica</i>	7
<i>Achnanthes wellsiae</i>	1A, 7
<i>Achnanthes</i> spp.	1A, 2A, 3, 4, 5, 7
<i>Anomoneis serians</i> v <i>brachysira</i>	3, 5, 7
<i>Amphora</i> cf <i>angusta</i> v <i>ventricosa</i>	2A, 6
<i>Amphora</i> cf <i>bigibba</i>	1A
<i>Amphora cocconeiformis</i>	1A, 2A, 3, 4
<i>Amphora ovalis</i>	1A, 4, 6
<i>Amphora subangularis</i>	2A
<i>Amphora</i> spp.	1A
<i>Bacillaria paradoxa</i>	1A, 2A, 3, 4, 5, 6
<i>Brebissonii</i> cf	2A, 3, 6, 7
<i>Caloneis</i> cf <i>alpestris</i>	5
<i>Caloneis amphisbaena</i> v <i>subsalina</i>	3
<i>Caloneis bacillum</i>	2A
<i>Caloneis</i> cf <i>limosa</i>	3
<i>Caloneis ventricosa</i>	7
<i>Cocconeis diminuta</i>	2A
<i>Cocconeis placentula</i>	3, 4, 5
<i>Cocconeis</i> spp.	2A, 6
<i>Coscinodiscus lacustris</i> v <i>septrionalis</i>	4
<i>Coscinodiscus</i> spp	2A, 4, 6
<i>Cyclotella menenghiana</i>	1A, 2A, 3, 4, 5, 6, 7
<i>Cyclotella</i> spp.	7
<i>Cymbella cuspidata</i>	2A, 5
<i>Cymbella</i> cf <i>gracilis</i>	3
<i>Cymbella lanceolata</i>	4, 7
<i>Cymbella</i> spp.	3, 4, 5
<i>Denticula elegans</i> cf <i>v valida</i>	5
<i>Denticula</i> cf <i>pelagica</i>	6
<i>Diatoma elongatum</i>	2A, 4, 5, 6, 7
<i>Diatoma</i> spp.	3, 6

<i>Diploneis bombus</i>	7
<i>Diploneis interruptus</i>	5, 6
<i>Diploneis ovalis</i>	2A, 4, 5, 6
<i>Diploneis</i> spp.	2A, 3
<i>Entomoneis</i> cf <i>costata</i>	6
<i>Entomoneis paludosa</i>	4
<i>Entomoneis robusta</i>	1A, 2A
<i>Entomoneis</i> spp.	1A, 4, 5
<i>Epithemia</i>	5
<i>Eunotia</i> cf <i>carolina</i>	2A
<i>Eunotia curvata</i> ( <i>lunaris</i> )	2A, 3, 4, 5, 6, 7
<i>Eunotia exigua</i>	2A
<i>Eunotia faba</i>	6
<i>Eunotia flexuosa</i>	3, 5
<i>Eunotia incisa</i>	5, 7
<i>Eunotia major</i>	6
<i>Eunotia monodon</i>	4, 5
<i>Eunotia pectinalis</i>	2A, 3, 4, 5, 6
<i>Eunotia pectinalis</i> v <i>minor</i>	4, 5, 7
<i>Eunotia pectinalis</i> v <i>recta</i>	5
<i>Eunotia veneris</i>	3, 6
<i>Eunotia</i> spp.	1A, 2A, 3, 5, 7
<i>Fragilaria brevistriata</i>	1A, 2A, 3, 4, 5, 6, 7
<i>Fragilaria</i> cf <i>capucina</i>	4, 5, 6
<i>Fragilaria construens</i>	2A, 3, 4, 5, 7
<i>Fragilaria construens</i> var <i>venter</i>	1A, 2A, 3, 4, 5, 6, 7
<i>Fragilaria virescens</i>	1A, 2A, 3
<i>Fragilaria virescens</i> v <i>exigua</i>	2A, 4, 5, 6, 7
<i>Frustulia creuzburgensis</i>	2A
<i>Frustulia rhomboides</i>	3
<i>Frustulia vulgaris</i>	6, 7
<i>Gomphonema acuminatum</i> v <i>brebissonii</i>	5
<i>Gomphonema gracile</i>	5
<i>Gomphonema</i> spp.	3, 4, 5, 7
<i>Gyrosigma</i> cf <i>balticum</i>	2A
<i>Gyrosigma</i> spp.	3, 4, 5, 6
<i>Mastogloia</i> spp.	4, 6
<i>Melosira granulata</i>	7
<i>Melosira italica</i>	3, 4, 5, 6, 7
<i>Melosira jurgensis</i>	1A, 2A, 3, 4, 5, 7
<i>Melosira nummuloides</i>	1A, 2A, 3, 4, 7
<i>Melosira</i> cf <i>sulcata</i>	7
<i>Melosira</i> cf <i>varians</i>	4, 5
<i>Melosira</i> cf <i>distans</i>	5
<i>Melosira</i> spp.	7

<i>Meridion circulare</i>	5, 7
<i>Navicula</i> cf <i>arvensis</i>	2A
<i>Navicula bacillum</i>	6
<i>Navicula bremensis</i>	3, 5
<i>Navicula cocconeiformis</i>	7
<i>Navicula crucicula</i>	2A, 3
<i>Navicula cryptocephala</i>	1A
<i>Navicula elegans</i>	1A, 3, 6, 7
<i>Navicula gastrum</i>	7
<i>Navicula halophila</i>	2A
<i>Navicula halophila</i> v <i>tenuirostris</i>	2A, 3
<i>Navicula hungarica</i>	2A, 3, 5, 7
<i>Navicula integra</i>	1A
<i>Navicula lacustris</i>	2A
<i>Navicula minima</i>	5
<i>Navicula peregrina</i>	6
<i>Navicula placenta</i>	7
<i>Navicula protracta</i>	2A
<i>Navicula pupula</i>	3, 5
<i>Navicula pusilla</i>	2A
<i>Navicula pseudofrickia</i>	6
<i>Navicula pygmaea</i>	1A, 2A, 3, 6
<i>Navicula radiosa</i> type	2A, 3, 5, 6
<i>Navicula salinarum</i>	2A, 3, 5, 6, 7
<i>Navicula</i> cf <i>sanctaecrucis</i>	1A
<i>Navicula seminuloides</i>	3
<i>Navicula spicula</i>	1A, 2A, 3, 4
<i>Navicula subhamulata</i>	1A
<i>Navicula</i> cf <i>subrhynchocephala</i>	6
<i>Navicula</i> cf <i>viridula</i>	6
<i>Navicula</i> cf <i>yarrensis</i>	2A, 3
<i>Navicula</i> spp.	1A, 2A, 3, 5, 6
<i>Neidium bisulcatum</i>	5
<i>Nitzschia amphibia</i>	1A, 3
<i>Nitzschia commutata</i>	5
<i>Nitzschia dissipata</i>	3, 6, 7
<i>Nitzschia dubia</i>	3
<i>Nitzschia gracilis</i>	5
<i>Nitzschia hantzschiana</i>	1A
<i>Nitzschia hungarica</i>	6
<i>Nitzschia ignorata</i>	2A
<i>Nitzschia linearis</i>	6
<i>Nitzschia littoralis</i>	2A, 6
<i>Nitzschia palea</i>	1A, 2A, 3, 5
<i>Nitzschia pusilla</i>	2A, 3, 4, 5, 6, 7
<i>Nitzschia recta</i>	4, 5
<i>Nitzschia scalaris</i>	1A, 2A, 3, 4, 6, 7
<i>Nitzschia sigma</i>	1A
<i>Nitzschia sigmoidea</i>	5
<i>Nitzschia tryblionella</i>	2A, 3, 6
<i>Nitzschia</i> spp.	2A, 4



<i>Opephora martyii</i>	5
<i>Pinnularia brebissonii</i>	2A
<i>Pinnularia latevittata</i>	3
<i>Pinnularia macilenta</i>	6
<i>Pinnularia cf major</i>	2A, 3
<i>Pinnularia cf socialis</i>	6
<i>Pinnularia spp.</i>	2A, 6
<i>Plagiotropis</i>	1A, 2A
<i>Pleurosigma</i>	2A, 5, 6, 7
<i>Rhopalodia cf gibberula</i>	2A, 6
<i>Stauroneis anceps f gracilis</i>	6
<i>Stauroneis cf parvula</i>	1A
<i>Stauroneis parvula v. prominula</i>	6
<i>Stauroneis phoenicenteron</i>	6
<i>Stauroneis salina</i>	4
<i>Stauroneis cf smithii</i>	2A
<i>Stephanodiscus spp.</i>	4
<i>Surirella cf moelleriana</i>	7
<i>Surirella cf ovalis</i>	6
<i>Surirella ovulum</i>	7
<i>Surirella spp.</i>	2A, 5
<i>Synedra acus</i>	1A, 2A, 3, 5
<i>Synedra delicatissima</i>	5, 6
<i>Synedra cf demerarae</i>	5
<i>Synedra fasciculata</i>	5, 6
<i>Synedra parasitica</i>	3, 4, 5, 7
<i>Synedra pulchella</i>	1A, 2A, 3, 4, 5, 6, 7
<i>Synedra rumpens</i>	2A, 3, 5
<i>Synedra rumpens v fragiloides</i>	1A, 2A, 3, 4, 5, 6, 7
<i>Synedra tabulata</i>	3, 4, 5
<i>Synedra ulna</i>	2A, 3, 4, 5, 6, 7
<i>Synedra cf ulna cf ramesi</i>	1A, 2A
<i>Synedra spp</i>	5, 6, 7
<i>Tabellaria fenestrata</i>	3, 4, 6, 7
<i>Tabellaria flocculosa</i>	2A, 3, 4, 6, 7
<i>Tabellaria spp.</i>	7



